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ABSOLUTE PRESSURE CALIBRATIONS OF MICROPHONES

By Richard K. Cook

ABSTRACT

A tourmaline-crystal disk was used both as a microphone (direct piezoelectric effect) and as a sound source (converse piezoelectric effect). Application of a principle of reciprocity to the acoustic measurements gave an absolute determination of the piezoelectric modulus $d_{33}+2d_{31}$ of tourmaline under hydrostatic pressure. A condenser microphone was calibrated by the tourmaline disk. The same principle was applied to data obtained by using a condenser microphone as both source and microphone to secure an absolute calibration of another condenser microphone. It was proved experimentally that the tourmaline disk and the condenser microphones satisfied the principle of reciprocity. The absolute acoustic determination of the piezoelectric modulus gave $d_{33}+2d_{31}=2.22\times10^{-17}$ coul/dyne. The "reciprocity" calibrations agreed with the results of electrostatic actuator, pistonphone, and "smoke particle" calibrations, but disagreed with thermophone calibrations of the condenser microphones.

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I. INTRODUCTION

Absolute measurements of sound intensity are of basic importance in acoustics. Such measurements are most conveniently made by means of calibrated microphones, and it is important to have accurate methods of making both absolute pressure and absolute free-field calibrations of microphones. Absolute pressure calibrations are needed at low frequencies to supplement free-field Rayleigh-disk measurements at higher frequencies, and are needed to check Rayleigh-disk measurements in the frequency region in which both pressure and free-field calibrations should be the same. Absolute pressure calibrations are also needed in audiometric work.

First calibrations of a condenser microphone made with an electrostatic actuator and with a thermophone, both of conventional design, showed a difference much greater than the probable error of the determination. The difference between the thermophone and the free-field Rayleigh-disk calibrations of a condenser microphone, in the

frequency region in which both calibrations should be the same, was also greater than the probable error. It was decided to use piezoelectric crystals to throw some light on the discrepancies between the results obtained with the thermophone, the electrostatic actuator, and the Rayleigh disk.

II. PRINCIPLE OF RECIPROCITY

1. GENERAL

Shortly after the discovery of the direct piezoelectric effect by the brothers P. and J. Curie, M. G. Lippmann predicted the existence of a converse piezoelectric effect, and showed quantitatively how large it should be.

Lippmann's proof, generalized by W. Voigt [1][1], is in reality a special case of a principle of reciprocity. Other special cases of the principle are well known in applied mechanics, electrical engineering, and acoustics. This principle was discussed by Lord Rayleigh [2] for mechanical systems and electrical systems, and was discussed by S. Ballantine [3] for certain mixed mechanical and electrical systems. The same principle of reciprocity can be applied not only to piezoelectric crystals but also to condenser microphones, moving-coil microphones, and to the thermophone. By means of this principle, the output of a transducer (i. e., a device which is used as both sound source and microphone) as a sound source can be computed from its response as a microphone, and vice versa.

Suppose that a pressure sinusoidal in time

$$p=p_0e^{i\omega t}$$

is applied to the diaphragm of a transducer (e. g., a condenser microphone); suppose electric charge

$$q=q_0e^{i\omega t}$$

is released from the transducer. The release of this charge, q, by the pressure, p, is called the direct effect (see fig. 1). It is assumed that the charge released is directly proportional to the pressure. This assumption of linearity is sufficient for the application of the reciprocity principle.

If the proportionality between p and q is given by

$$q=\tau p, \tag{1}$$

the principle of reciprocity asserts that

$$v=\tau u, \tag{2}$$

where τ is numerically the same in both eq 1 and 2, if q, p, v, and u are all in the same system of units, and where

$$v=v_0e^{i\omega t}$$

[1] Figures in brackets indicate the literature references at the end of this paper.

is the change of volume caused by the motion of the diaphragm due to an applied voltage

$$u = u_0 e^{i\omega t}.$$

The volume change, v, due to the voltage, u, is called the converse effect (see fig. 2). There might be differences in phase among the quantities q, p, v, and u. To account for phase differences, the

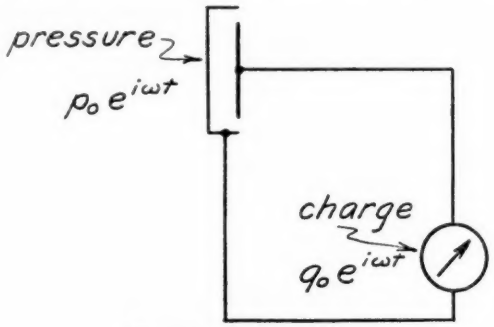

FIGURE 1.—*Direct effect.*
Transducer used as microphone.

coefficients q_0, p_0, v_0, and u_0, and the transduction coefficient, τ, are in general complex numbers, and τ might also be a function of frequency.

The principle of reciprocity applies without regard to the mechanism of operation of the transducer, provided only it is linear. The principle applies even if there are frictional forces or thermal actions in the

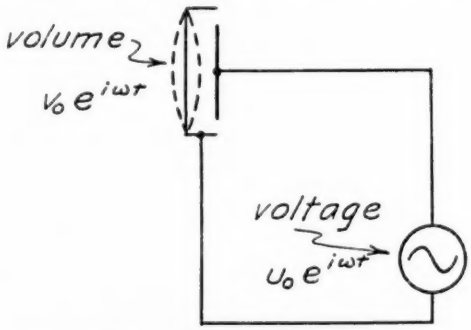

FIGURE 2.—*Converse effect.*
Transducer used as sound source.

transducer, provided these are linear (i. e., $\tau = q/p$ is independent of p). Thus a thermophone without a polarizing current is not linear when used as a sound source and the principle does not apply. Indeed, the thermophone used as a microphone under such circumstances has no response. But with a polarizing current the thermophone becomes a linear sound source (within certain limits), and the reciprocity theorem can be applied within these limits to compute the response as

a microphone from the output of the thermophone as a source of sound. Similarly, the principle can be applied to a condenser microphone having a polarizing voltage, but the principle is not applicable to an unpolarized condenser microphone.

Besides the assumption of linearity, it is also assumed that the only force applied in the direct effect is the pressure on the diaphragm (i. e., the electric terminals of the transducer are shorted, so that no electric forces are applied), and that the only force applied in the converse effect is the voltage on the electric terminals (i. e., the diaphragm volume change takes place with no reaction from the gas in front of the diaphragm). It presently will be shown how closely these conditions are realized in the laboratory, and how to take into account departures from the specified conditions.

If p and v are, respectively, in dynes per square centimeter and cubic centimeter and Q and E in coulombs and volts, then eq 1 and 2 become, in this mixed system of units,

$$\left.\begin{aligned} Q&=\tau p \\ v&=10^7\tau E \end{aligned}\right\} \tag{3}$$

and τ is in square centimeters coulomb per dyne. These units will be used throughout the remainder of this article. The quantities representing voltage, charge, pressure, and volume changes will henceforth have root-mean-square (rms) values.

2. APPLICATION TO PIEZOELECTRIC CRYSTALS

Tourmaline, a polar crystal of the trigonal system, acquires a uniform electric moment per unit volume under hydrostatic pressure. The magnitude of the moment per cubic centimeter is

$$M=(d_{33}+2d_{31})p \text{ coul/cm}^2,$$

and its direction is parallel to the principal (optic and piezoelectric) crystal axis. The quantities d_{33} and d_{31} (Voigt's [1] notation) are, respectively, the piezoelectric modulus for normal pressures on faces perpendicular to the principal axis, and a piezoelectric modulus for normal pressures on any two faces which are parallel to the principal axis and to each other. The quantity $d_{33}+2d_{31}$ is the piezoelectric modulus of the crystal under hydrostatic pressure.

Voigt's measurements on Brazilian tourmaline gave

$$d_{33}+2d_{31}=2.42\times10^{-17} \text{ coul/dyne}.$$

For a crystal cut in the shape of a circular disk of area A and having its parallel flat faces perpendicular to the principal axis, the electric moment per unit volume, M, will appear as a uniform electric charge per unit area, M, on the flat faces, or the total charge on each flat face will be

$$Q=AM=A(d_{33}+2d_{31})p \text{ coul}.$$

Then, by the principle of reciprocity, a potential difference of e'_s (volts) applied between the flat faces will cause a volume change of the crystal of amount

$$v=10^7A(d_{33}+2d_{31})e'_s \text{ cm}^3. \tag{4}$$

A tourmaline crystal is then used in the following way as both sound source and microphone to secure an absolute pressure calibra-

tion of (for example) a condenser microphone, and to secure also the hydrostatic piezoelectric modulus of the crystal.

Let the response of the condenser microphone be

$$\rho = \frac{e_m}{p} \text{cm}^2 \text{ volts/dyne},$$

where e_m is the voltage output of the microphone due to the sound pressure, p. The response of the crystal used as a microphone (direct effect) is

$$\frac{A(d_{33}+2d_{31})}{C} = \frac{Q}{Cp} \text{ cm}^2 \text{ volts/dyne},$$

where C (farads) is the capacity of the crystal microphone. The crystal response is expressed in this way because Q/C (the voltage output of the crystal microphone) can be readily measured, whereas it is not feasible to measure Q directly.

The first step is to measure the ratio of the condenser-microphone response to the crystal-microphone response. The ratio is

$$\frac{\rho C}{A(d_{33}+2d_{31})} = \frac{e_m}{e_s}, \tag{5}$$

and is got experimentally by applying the same pressure (or pressures in a known ratio) to both microphones and by measuring the ratio of the output voltages, e_m/e_s, by means of an attenuation box or known resistances. The voltage output of the condenser microphone is e_m, and that of the crystal for the same sound pressure is e_s.

The second step is to use the crystal as a source, acting on the condenser microphone as a microphone through a gas-filled cavity of volume, V (cm^3). If B (dynes/cm^2) is the barometric pressure in the gas and γ is the ratio of specific heats of the gas, then the piezoelectric volume change of the crystal given by eq 4 will give rise to a pressure

$$p = \left(\frac{10^7 \gamma B}{V}\right) A(d_{33}+2d_{31}) e'_s \text{ dynes/cm}^2,$$

provided v is small in comparison with V. The condenser microphone voltage output due to this pressure will be

$$e'_m = \left(\frac{10^7 \gamma B}{V}\right) A(d_{33}+2d_{31}) \rho e'_s \text{ volts}. \tag{6}$$

Simultaneous solution of eq 5 and 6 yields

$$\left.\begin{aligned} \rho &= \sqrt{\frac{10^{-7} V}{\gamma B C}\left(\frac{e_m}{e_s}\right)\left(\frac{e'_m}{e'_s}\right)} \text{ cm}^2 \text{ volts/dyne} \\ A(d_{33}+2d_{31}) &= \sqrt{\frac{10^{-7} C V}{\gamma B}\left(\frac{e_s}{e_m}\right)\left(\frac{e'_m}{e'_s}\right)} \text{ cm}^2 \text{ coul/dyne} \end{aligned}\right\}. \tag{7}$$

Thus an absolute pressure calibration of a condenser microphone is obtained by absolute measurements of a volume, the barometric pressure, and a capacitance, and by measurements of two voltage ratios. An absolute determination of the adiabatic piezoelectric modulus of the tourmaline crystal under hydrostatic pressure is obtained by measurement of the crystal area in addition to the quanti-

ties enumerated above. The only quantity which is not measured directly is γ, whose values for air, hydrogen, and helium are accurately known.

Superimposed on the piezoelectric action in the direct effect will be the pyroelectric effect (since temperature changes in the gas which accompany pressure changes will penetrate into the crystal), and superimposed on the piezoelectric action in the converse effect will be the electrocaloric effect (since temperature changes in the crystal which accompany voltage changes will penetrate into the gas). But the principle of reciprocity will hold nevertheless, and eq 7 will give a quantity which represents a mixed piezoelectric and thermoelectric modulus at low frequencies, and which will approach asymptotically the adiabatic piezoelectric modulus at high frequencies.

In cavities of small volume, the elastic volume changes of the crystal (used as a microphone) due to an applied pressure, will in themselves give rise to a pressure superimposed on the applied pressure calculated on the assumption of no yielding of the crystal. The crystal suffers a volume change also if the faces are not at the same potential, because the potential difference, Q/C, acquired by the crystal causes a piezoelectric volume change by virtue of the converse effect, and likewise will give rise to a pressure superimposed on the calculated applied pressure. In effect, the piezoelectric modulus will appear to be a function of cavity volume, if the crystal volume changes are appreciable and due allowance is not made for them. This will be called the volume effect. For tourmaline the adiabatic compressibility is about 10^{-12} cm^2/dyne. Therefore, the ratio of the pressure caused by elastic volume change to the applied pressure is less than 10^{-6} for cavity volumes greater than 10 cm^3 and crystal volumes less than 4 cm^3. For tourmaline the adiabatic piezoelectric modulus is about 2.4×10^{-10} cm/volt. Therefore, the ratio of the pressure caused by piezoelectric volume change to the applied pressure is less than 10^{-8} for cavity volumes greater than 10 cm^3, crystal areas less than 15 cm^2, and crystal-microphone capacitance greater than 30×10^{-12} farad. With these restrictions, the volume effect for a tourmaline crystal used as a microphone is completely negligible, and by the principle of reciprocity the volume effect for a tourmaline crystal used as a source is also negligible, with the same restrictions. The volume effect for condenser microphones will be discussed in section 3.

Quartz and Rochelle salt have no electric moment under hydrostatic pressure. This conclusion is reached from considerations of the crystal symmetry of these materials. Consequently, such crystals cannot be used in the same way as tourmaline is used to obtain an absolute calibration of a microphone.

3. APPLICATION TO CONDENSER MICROPHONES

Let ρ_1(cm^2 volts/dyne) be the response and C_1 (farads) the capacitance of a condenser microphone, *I*, which is to be used as both source and microphone to calibrate a second condenser microphone, *II*, whose response is ρ_2(cm^2 volts/dyne). The equations of the direct and converse effects for the condenser microphone are

$$\left.\begin{aligned} Q&=\rho_1 C_1 p \\ v&=10^7\rho_1 C_1 E \end{aligned}\right\}. \tag{8}$$

These correspond to eq 3. Microphone *I* is then used in exactly the same way as was the tourmaline crystal to secure an absolute pressure calibration of microphone *II*. That is to say, the first step is to obtain the ratio of the responses, ρ_1/ρ_2, by applying the same pressure to both microphones, and the second step is to couple microphone *I* (used as a sound source) to microphone *II* by means of a gas-filled cavity of known volume, from which is obtained the product of the responses, $\rho_1\ \rho_2$. The final equations for the responses, ρ_1 and ρ_2, are

$$\left.\begin{aligned}\rho_1 &= \sqrt{\frac{10^{-7}V}{\gamma BC_1}\left(\frac{e_1}{e_2}\right)\left(\frac{e'_2}{e'_1}\right)}\ \text{cm}^2\ \text{volts/dyne}\\ \rho_2 &= \sqrt{\frac{10^{-7}V}{\gamma BC_1}\left(\frac{e_2}{e_1}\right)\left(\frac{e'_2}{e'_1}\right)}\ \text{cm}^2\ \text{volts/dyne}\end{aligned}\right\} \tag{9}$$

These correspond to eq 7. In these equations V (cm^3) is the volume of the cavity in which microphone *I* is used as a sound source, B (dynes/cm^2) is the barometric pressure in the cavity, γ is the ratio of the specific heats of the gas in the cavity, e_1 and e_2 are, respectively, the voltage outputs of microphones *I* and *II* for the same applied pressure, and e'_2 is the voltage output of microphone *II* for a voltage e'_1 applied to microphone *I* when used as a sound source (the two microphones being coupled by the cavity of volume V).

The condenser microphone diaphragm suffers a volume change if the potential difference between the diaphragm and back plate is not steady, because the alternating potential difference, Q/C, causes a volume change by virtue of the converse effect, and will therefore give rise to a pressure superimposed on the applied pressure calculated on the assumption of no volume change of the microphone. The ratio of the pressure caused by this volume change to the applied pressure is less than 5×10^{-3} for a condenser microphone having a response less than 3×10^{-3} cm^2 volt/dyne and a capacitance less than 3.5×10^{-10} farad, and for cavity volumes greater than 10 cm^3. This part of the volume effect was therefore neglected.

The compressibility (admittance) of the diaphragm gives rise to a volume effect which is not negligible. An absolute calculation of the amount would require an exact knowledge of the construction of the microphone. In the absence of such knowledge, the amount of the volume effect must be determined experimentally by making response measurements at several different cavity volumes. Unfortunately, at high-frequencies volume effects due to cavity resonances swamp those due to diaphragm compressibility, and there is no way of separating the two effects. This means that a precise determination of the volume effect can be made only at low frequencies. Let the compressibility of the diaphragm *II* be $c_2(\text{cm}^5/\text{dyne})$; that is, a pressure of $p(\text{dynes/cm}^2)$ on the diaphragm causes a volume change of $c_2p(\text{cm}^3)$. Then at frequencies less than the lowest natural frequency of diaphragm *II* the compressibility will have the effect of increasing the cavity volume which appears in eq 9 from V to $V+\gamma Bc_2$. It is clear from the principle of reciprocity that the same volume effect will be present when the microphone is used as a sound source. If c_1 is the compressibility of diaphragm *I*, then the total effect will be to increase

the volume which appears in eq (9) from V to $V+\gamma Bc_1+\gamma Bc_2$. The quantity $\gamma Bc(\text{cm}^3)$ will hereafter be denoted by $\kappa(\text{cm}^3)$, and will be called the volume constant of the microphone.

III. EXPERIMENTAL RESULTS

1. REVERSIBILITY OF TRANSDUCERS

A "reversible" transducer is one which satisfies the principle of reciprocity. A simple experimental way of ascertaining whether or not two transducers are reversible is the following. The transducers are coupled by a cavity of fixed volume. A voltage e_1 is applied to transducer *I* (source), and the corresponding voltage output e'_2 of transducer *II* (microphone) is measured. Then a voltage e_2 is applied to transducer *II* (source), and the corresponding voltage output e'_1, of transducer *I* (microphone) is measured. Then the over-all coupled system is reversible, if the equation

$$\frac{C_2}{C_1}=\left(\frac{e_1}{e'_2}\right)\left(\frac{e'_1}{e_2}\right) \tag{10}$$

is satisfied, where C_2 and C_1 are the capacitances of transducers *II* and *I*, respectively. Thus eq10 is a necessary condition for the reversibility of each transducer. If a third transducer is used and eq10 holds for each pair of transducers, this will be a sufficient condition for the reversibility of each of the three. Actually, it will be entirely safe to assume each of two transducers is reversible if eq10 holds when the two transducers are coupled. Thus the reversibility of a transducer is determined experimentally by purely electrical measurements of two voltage ratios and a capacitance ratio.

Such measurements were made on the following: A Western Electric condenser microphone type 394, No. 4829 (denoted hereafter as microphone 2); a Western Electric condenser microphone type D96436, No. 70 (denoted hereafter as microphone 70); a tourmaline crystal transducer (denoted hereafter as transducer *CD*). Transducer *CD* was made of black California tourmaline, 3.8 cm in diameter and 0.3 cm in thickness. The front face was coated with tin foil affixed with wax, and the tourmaline was wrung on to a brass block. The block was insulated from the outside brass block (at ground potential) which was connected to the tin foil.

The voltage ratios appearing in eq10 were measured at various frequencies by means of an attenuation box to the nearest decibel and by means of an output meter to the nearest one-tenth decibel. The capacitances were separately measured at 1,000 c/s (by means of a strict substitution method) with a variable capacitance calibrated in the capacitance section of this Bureau. The results are shown in figure 3. The gases which were used with each pair of transducers are indicated in the legend. The sound pressure was about 2×10^{-2} dyne/cm^2 with the tourmaline transducer *CD* as source, and about 10 dynes/cm^2 with transducer *CD* as microphone. In the other two cases plotted in figure 3, the pressure was about 1 dyne/cm^2.

The estimated probable error in 20 $\log_{10}$ (C_2/C_1) is 0.1 db, and in 20 $\log_{10}$ (e_1/e'_2) (e'_1/e_2) is less than 0.2 db. The conclusion from the results plotted in figure 3 is, that within the experimental uncertainty

eq10 is satisfied. Consequently, condenser microphones 2 and 70 and tourmaline transducer *CD* are reversible. This is a direct experimental proof of the equality of the direct and converse piezoelectric moduli in tourmaline under hydrostatic pressure.

After Lippmann's theoretical proof of the equality of the direct and converse piezoelectric moduli, J. and P. Curie made an attempt to verify the equality for the modulus, d_{11} in quartz, but experimental difficulties enabled them to obtain only a very rough agreement between the two moduli. Since then, H. Osterberg and J. W. Cookson [4] have concluded that measurements of d_{11} by some observers who used the direct effect only have agreed on the whole with measurements of d_{11} by other observers who used the converse effect only.

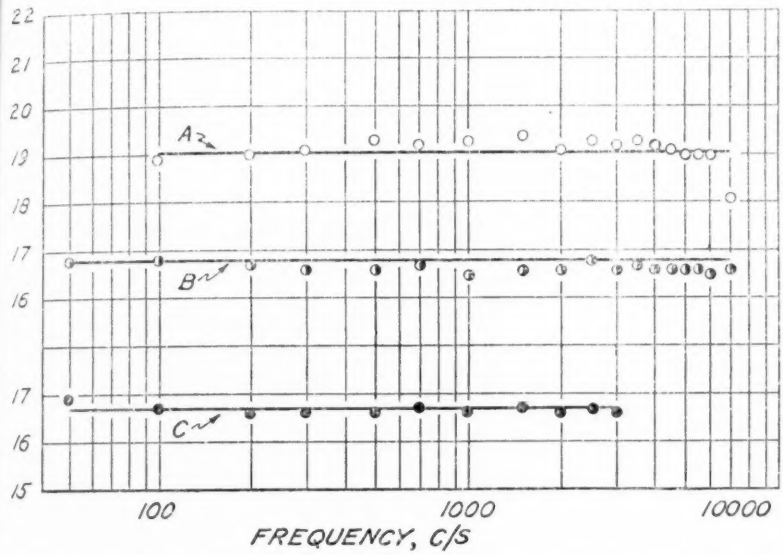

FIGURE 3.—*Graph showing reversibility of tourmaline transducer and condenser microphones.*

○=20 $\log_{10}$ (e_1/e'_2) (e'_1/e_2), and curve A=20 $\log_{10}$ (C_2/C_1) at 1,000 c/s, for condenser microphone 2 and tourmaline transducer *CD*, in helium.

◑=20 $\log_{10}$ (e_1/e'_2) (e'_1/e_2), and curve *B*=20 $\log_{10}$ (C_2/C_1) at 1,000 c/s, for condenser microphones 2 and 70, in helium.

●=20 $\log_{10}$ (e_1/e'_2) (e'_1/e_2), and curve *C*=20 $\log_{10}$ (C_2/C_1) at 1,000 c/s, for condenser microphones 2 and 102, in air.

Because of variations in the composition of tourmaline from different sources, it is not possible, in order to decide the equality of the two moduli for tourmaline, to compare the results of some observers who used the direct effect only with the results of other observers who used the converse effect only.

2. MICROPHONE CALIBRATIONS

The reversibility of condenser microphones 2 and 70 and of transducer CD having been established, the principle of reciprocity was applied to data obtained with these transducers to secure absolute pressure calibrations of microphones 2 and 70.

The results are shown in figures 4 and 5. The reciprocity calibrations are those obtained with condenser microphone 2 used as both source and microphone. The cavity volumes and gases which were used are indicated in the legends. The estimated probable error of measurement is 0.2 db. The volume effects of the microphone diaphragms and the cooling effect of the walls of the cavity have not been included in the responses, which were computed directly from eq 9 (the geometrical volume of the cavity being used for V). These omissions introduce systematic errors not much greater than the probable error stated above. The amounts of these are deduced in the following paragraph.

Measurements of the volume constant, κ, gave $\kappa_2=1.3 \pm 0.2$ cm^3, and $\kappa_{70}=0.3 \pm 0.2$ cm^3. These values are experimentally the same in air, hydrogen, and helium, and are experimentally independent of whether the sound source used in the measurements is a thermophone, a tourmaline crystal, or a condenser microphone. Measurements from which the above values of κ are obtained were made usually at cavity volumes of 15, 30, and 40 cm^3. The fact that the thermophone yields the same value for κ as does the other sound sources is surprising, since Ballantine [5] has shown that the diaphragm motion of a condenser microphone should react on the thermophone foil strips in such a way as to result in a net effect different for different gases and in any case much smaller than the experimental value found above for condenser microphone 2. The value of κ_2 found above is also somewhat greater than the value computed by L. J. Sivian [6] for microphones of the same type. Direct measurements of cos ϕ (where ϕ is the phase angle between the pressure applied to the microphone diaphragm and the voltage output of the microphone) showed that the values of κ_2 and κ_{70} are practically independent of frequency below 3,000 c/s. Because of the difficulty of measuring κ above about 3,000 c/s (although the results of the measurements of cos ϕ show that κ_2 and κ_{70} become zero at about 6,000 c/s and become negative at higher frequencies), it was decided to make the reciprocity measurements at cavity volumes of 40 cm^3 so as to keep the volume effects small. Omission of the volume effects means that the computed response of microphone 2 is low by 0.3 db and of microphone 70 is low by 0.1 db below 3,000 c/s. The cooling effect of the walls of the cavity must also be considered. It is usually incorrectly assumed that the temperature variation of the gas at the walls of the cavity is zero, on the grounds that the thermal conductivity of the metal walls is much greater than that of the gas. However, in a quasi-stationary temperature distribution (all temperatures sinusoidal functions of the time) the quantity of importance is the thermal diffusivity, which is the thermal conductivity divided by the product of density and specific heat. The thermal diffusivities of brass, air, hydrogen, and helium are, respectively, at room temperature and barometric pressure 0.34, 0.28, 1.67, and 1.78 cm^2 sec. From these values it can be deduced that a better boundary condition at the walls of the cavity is that the rms temperature at the walls is one-half the rms temperature in the gas at a distance from the walls. The inclusion of this boundary condition in the reciprocity calibrations raises the computed responses of microphones 2 and 70 by less than 0.1 db, for frequencies greater than 50 c/s and a cavity volume of 40 cm^3, and for any of the three gases mentioned above. The upshot of all the fore-

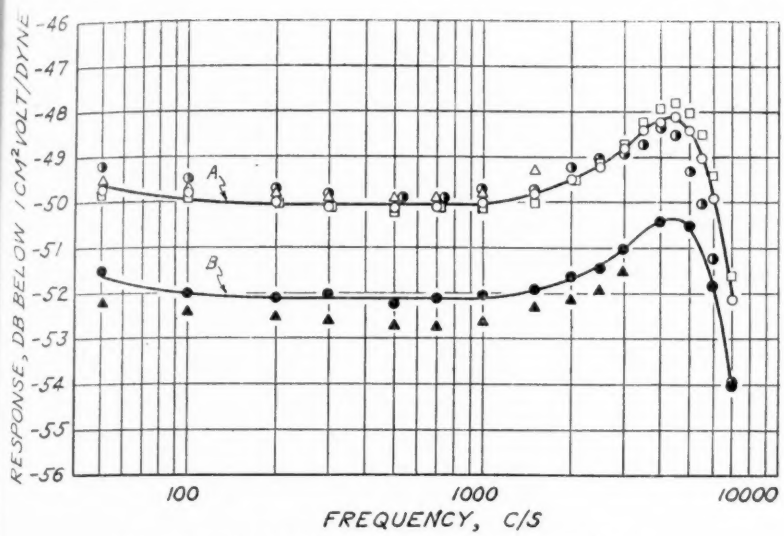

FIGURE 4.—*Calibration graph of condenser microphone 2.*

○ and curve *A* = reciprocity in hydrogen, cavity volume 40 cm³.
△ = reciprocity in air, cavity volume 40 cm³.
□ = reciprocity in helium, cavity volume 40 cm³.
◑ = electrostatic actuator.
● and curve *B* = thermophone in hydrogen, cavity volume 8.5 cm³.
▲ = thermophone in air, cavity volume 8.5 cm³.

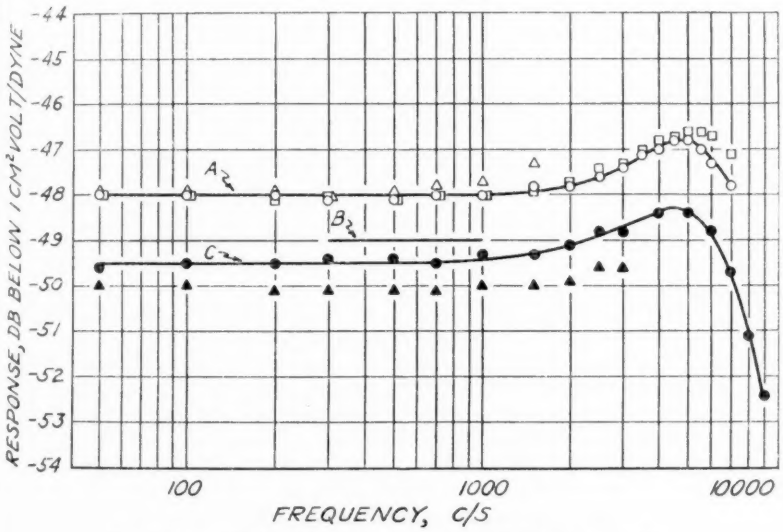

FIGURE 5.—*Calibration graph of condenser microphone 70.*

○ and curve *A* = reciprocity in hydrogen, cavity volume 40 cm³.
△ = reciprocity in air, cavity volume 40 cm³.
□ = reciprocity in helium, cavity volume 40 cm³.
Curve B = Rayleigh disk.
● and curve *C* = thermophone in hydrogen, cavity volume 10.8 cm³.
▲ = thermophone in air, cavity volume 10.8 cm³.

going is that the systematic errors introduced into the reciprocity calibrations by omission of the volume effects and cooling effects amount to a lowering of the response of microphone 2 by 0.3 db and of microphone 70 by 0.1 db.

The reciprocity calibrations of condenser microphones 2 and 70 obtained with the tourmaline transducer *CD* used as both sound source and microphone agree (within the estimated probable error) with the reciprocity calibrations obtained with the condenser microphone 2 used as both sound source and microphone.

Figure 4 shows also the results of electrostatic actuator calibrations of microphone 2. The actuator measurements were made with a "solid" grille having 25 holes each 0.7 mm in diameter and 3 mm long, and with a slotted grille having grille bars each 1.53 mm wide and 3 mm deep and grille slots each 0.88 mm wide. The pressure produced by the slotted grille was computed by means of nomographs made for such grilles by S. Ballantine [5]. The results with the slotted grille at frequencies higher than 1,000 c/s are plotted, in spite of the presence of numerous small "resonances" which appeared in the output of microphone 2 and which vitiate the results at such frequencies. Below 1,000 c/s the electrostatic actuator calibrations and the reciprocity calibrations in air, hydrogen, and helium of condenser microphone 2 all agree within the estimated probable error.

Figures 4 and 5 also show the results of gold foil thermophone calibrations of condenser microphones 2 and 70. The thermophone results were computed with the formula given by S. Ballantine [5], except for minor corrections which will be presently discussed. The thermophone cavity volumes are about the sizes used by several other observers. The estimated probable error of the individual thermophone determinations below 1,000 c/s is 0.2 db, but the estimated probable error of the difference between the air and hydrogen calibrations of a particular microphone is less than 0.2 db. The response obtained by the thermophone of a microphone of the same type as No. 2 had a value 0.3 db lower in helium than in air. It is plain that the thermophone calibrations in air, hydrogen, and helium disagree among themselves and disagree with the reciprocity calibrations in the regions of safe comparison below 1,000 c/s by amounts much greater than the probable errors of the differences. The inclusion of the volume effects will increase the responses of both microphones 2 and 70 below 3,000 c/s, so that the thermophone calibrations in air (which are more reliable than those in hydrogen and helium because of smaller systematic errors) will be below the reciprocity calibrations by 1.5 db for each microphone. This difference is still much greater than the estimated probable error. The disagreement between the thermophone calibrations in air, hydrogen, and helium is unchanged by inclusion of the volume effects.

The thermophone formula and calculations given by S. Ballantine [5] require correction because they are based on the assumption of no temperature variation in the gas at the walls of the cavity (this assumption was discussed above) and on the assumption that commercial gold foil has the same specific heat as pure gold. The specific heat of the gold foil, calculated from the results of a chemical assay, was 0.0328 cal/g° C, whereas that of pure gold is 0.0313 cal/g° C. The two corrections are in opposite directions and almost nullify one

another, thus leaving calculations made from Ballantine's thermophone formula practically unchanged.

Pistonphone measurements were made by Guy Cook and the author on a condenser microphone of the same type as microphone 2. The measurements were made between 50 and 200 c/s in a cavity of 15 cm^3 at a sound pressure of about 5 dynes/cm^2. Air, hydrogen, and helium were used. The piston was driven by a loudspeaker coil, and its amplitude of motion was measured by means of an optical lever and autocollimator. The amplitude measurements were checked by a microscope having a calibrated graticule. The computed probable error of the pistonphone results was 0.3 db, and the results agreed with an electrostatic actuator calibration of the same microphone within the probable error.

Resonant-tube measurements were made by Guy Cook and the author on the same condenser microphone. The microphone was placed at one end of the resonant tube. The amplitude of motion of illuminated tobacco-smoke particles was observed (with a microscope having a calibrated graticule) at the central displacement loop in the gas in the resonant tube. Observations were made at 95 and 285 c/s at a sound pressure of about 75 dynes/cm^2. The estimated probable error of the resonant tube results was 0.5 db, and the results agreed with the electrostatic actuator calibration of the same microphone within the estimated probable error.

The disk curve *B* in figure 5 is placed 0.5 db above the thermophone calibration in hydrogen, and is the result of Rayleigh-disk and thermophone comparisons between 300 and 1,000 c/s on several other microphones of the same type as microphone 70. The Rayleigh-disk measurements were made in the free field by Guy Cook.

The conclusion is, that in the usually accepted thermophone formula there are systematic errors which are different for different gases, and which are much greater than the error of measurement. The trouble probably lies in the assumed modus operandi of the thermophone. It has been suggested that the gold foil possibly adsorbs and emits gas during each thermal cycle. Another suggestion is, that viscosity forces have an effect on the pressure produced by the thermophone. The computed responses in air, hydrogen, and helium are in the same order as the viscosity coefficients of these gases.

3. PIEZOELECTRIC MODULI

The results of acoustic measurements, based on the principle of reciprocity, of the adiabatic piezoelectric modulus $d_{33}+2d_{31}$ of California tourmaline are shown in figure 6. The tourmaline was crystal *CD*, which was used as both source and microphone.

The results of static testing-machine measurements (by use of the direct effect) of the modulus d_{33} and Voigt's [1] static measurements (also by use of the direct effect) on Brazilian tourmaline are also given in figure 6. The frequency scale of the abscissas does not apply to the horizontal lines representing the static tests; these lines were drawn merely to facilitate comparisons with the acoustic measurements. Static measurements yield isothermal moduli, whereas the acoustic measurements yield adiabatic moduli. However, D. A. Keys [7] has shown from thermodynamic considerations that the difference between the isothermal and adiabatic moduli is less than

0.3 percent. Below 500 c/s the acoustic measurements do not yield the adiabatic modulus, since the droop in the measured modulus $d_{33}+2d_{31}$ at low frequencies is due to the superposition of thermoelectric effects on the piezoelectric action. The droop above 3,000 c/s is caused by cavity resonances.

The testing-machine measurements of the modulus d_{33} were made at loads between 1,000 and 3,000 lb in a hydraulic testing machine. A preassigned load was applied to a crystal disk 3.8 cm in diameter and 0.15 cm thick, and the electric charge released from the crystal on sudden release of the testing-machine load was measured by a calibrated ballistic galvanometer. A check of the experimental setup

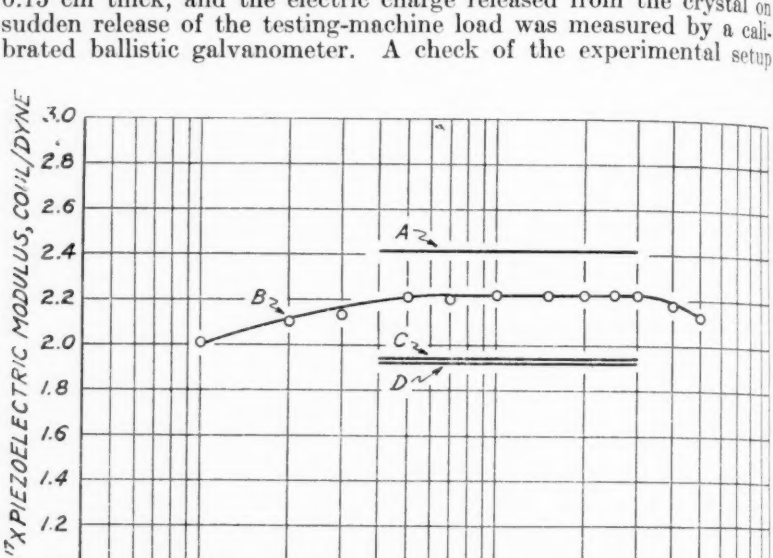

FIGURE 6.—*Graph of piezoelectric moduli of tourmaline.*

○ and curve B=acoustic measurements of $d_{33}+2d_{31}$ for California tourmaline.
Curve A=static measurements by Voigt of $d_{33}+2d_{31}$ for Brazilian tourmaline.
Curve C=static testing-machine measurements of d_{33} for California tourmaline.
Curve D=static measurements by Voigt of d_{33} for Brazilian tourmaline.

was made by measuring the piezoelectric modulus d_{11} of quartz, which is well known. The estimated probable error in the measured value of the modulus d_{33} for black California tourmaline is 2 percent.

The curious discovery was made that it is absolutely essential to load the crystal through rigid (e. g., steel) bearing blocks. Erroneous results were obtained when the tourmaline and quartz were loaded through Plexiglass (a methacrylate resin of low modulus of elasticity) bearing disks. It was established that these anomalies were not due to friction. Evidently the crystal is subjected to thermal actions and to large shearing stresses (in addition to the compressive stresses) when loaded through Plexiglass disks in contact with the crystal, and these thermal actions and shearing-stresses cause the anomalous piezoelectric effects.

The following measurements were made on California tourmaline, used as a sound source, in addition to the measurements of $d_{33}+2d_{31}$ given in figure 6. Three crystals (each 3.8 cm in diameter and 0.15

cm thick) cut from the same batch of tourmaline had identical piezoelectric moduli. When two of these disks were wrung together with vaseline so that the analogous ends of their crystal axes pointed in the same direction, the piezoelectric modulus was the same as that of a single disk, which shows that the acoustically measured modulus is independent of the crystal thickness. When the same two disks were wrung together so that the analogous ends of their axes pointed in opposite directions, the piezoelectric modulus was zero. Each disk suffered a volume change under the applied voltage, but the net volume change was zero, since the individual volume changes differed in phase by π. The piezoelectric modulus was independent of applied voltage in the range from 130 to 1,300 volts. The foregoing measurements were made in air, between 200 and 1,000 c/s, in a cavity of about 20-cm^3 volume. It is understood that the conclusions are valid only within the experimental uncertainty, which is about 2 percent of the modulus $d_{33}+2d_{31}$. In addition, a determination of the volume constant, κ, for a crystal yielded $\kappa=0$, within the experimental uncertainty of about 0.3 cm^3, which confirms the theoretical conclusion that a crystal used as a transducer should have no detectable volume effect.

A quartz-crystal disk, 3.6 cm in diameter and 0.46 cm thick, having its flat faces perpendicular to one of the three diagonal axes of the quartz, was used as a sound source in a cavity of about 20 cm^3. The measured piezoelectric modulus was about 1 percent of that of tourmaline at 500 c/s. At lower frequencies the disk had a small sound output, evidently due to electrocaloric effects superimposed on the piezoelectric. The conclusion is, that within the experimental uncertainty, the piezoelectric modulus of quartz under hydrostatic pressure is zero. This confirms experimentally the theoretical conclusion reached from considerations of crystal symmetry.

IV. INSTRUMENTS AND TECHNIQUE

The cavities were made of simple geometrical shapes (e. g., right circular cylinders), and the volumes were computed from measurements of the linear dimensions. The scale and micrometer calipers used in these measurements were compared with secondary standards kept in this Bureau. The estimated probable error in the measurement of volume is 0.4 percent.

The barometric pressure was measured by an aneroid barometer which from time to time was compared with a mercury barometer. The estimated probable error in the measurement of pressure by the aneroid barometer is 0.1 percent.

Microphone capacitances were measured by a strict substitution method. A variable air condenser, calibrated in the capacitance section of this Bureau, was used as a secondary standard. As a check on the technique, a particular condenser was measured in both the sound chamber and in the capacitance section. The estimated probable error in capacitance measurement is about 1 percent.

Voltage ratios were measured by means of an attenuation box to the nearest decibel, and by a copper oxide rectifier output meter to the nearest 0.1 db. The attenuation box was calibrated by comparison with a calibrated potentiometer, and had errors less than 0.1 db. The estimated probable error in the measurement of voltage ratio is

0.1 db. The output meter was used over a range not exceeding 0.5 db.

Nearly all the experimental measurements were made at room temperatures between 20° and 25° C, and at barometric pressures between 742 and 758 mm Hg. Within these limits there was no dependence of the responses of the condenser microphones on temperature or barometric pressure. Small variations in the responses (about 0.5 db in range) seemed to be entirely random in character.

Various tricks of technique were used to detect and eliminate spurious voltages in the microphone circuit. Such voltages are the commonest cause of trouble. For example, electrostatic coupling between the gold foil of the thermophone and the high-potential side of the tourmaline microphone causes a spurious voltage in the tourmaline-microphone voltage output. This will easily occur because the voltage applied to the thermophone is about 10^4 times greater than the voltage output of the tourmaline microphone. In another case, resistance coupling between the tourmaline-crystal sound-source circuit and the low-potential (ground) side of the condenser microphone causes a spurious voltage in the condenser-microphone voltage output. This might happen because the voltage applied to the crystal source is about 10^6 times greater than the voltage output of the condenser microphone. Reversal of the polarizing voltage on the condenser microphone (or, in the case of the thermophone, reversal of the polarizing current) will change the phase of the spurious voltage with respect to the voltage generated in the microphone by π, and the voltage output of the microphone will not be independent of polarity (as it should be), if the spurious voltage is appreciable. In crystal measurements, substitution of a dummy glass (or any nonpiezoelectric material) transducer for the crystal transducer will readily reveal spurious voltages.

V. SUMMARY

Application of a general principle of reciprocity to the action of a piezoelectric crystal or to a microphone yields absolute pressure calibrations of another microphone, and also yields absolute values of the adiabatic piezoelectric modulus under hydrostatic pressure. Absolute measurements of a volume, the barometric pressure and a capacitance are needed in addition to measurements of two voltage ratios; also, the ratio of specific heats of the gas used in the cavity is required.

Calibrations secured in this way are in good agreement with electrostatic actuator, pistonphone, and "smoke particle" calibrations of a condenser microphone. Thermophone calibrations in air, hydrogen, and helium disagreed among themselves and with the reciprocity calibrations of the same microphones by amounts much greater than the experimental uncertainty.

Absolute acoustic measurements of the adiabatic piezoelectric modulus of black California tourmaline under hydrostatic pressure gave $d_{33}+2d_{31}=(2.22\pm0.06)\times10^{-17}$ coul/dyne. It was experimentally proved that the direct and converse piezoelectric moduli $d_{33}+2d_{31}$ are equal, within the experimental uncertainty.

The following is a tentative set-up for securing absolute pressure calibrations of condenser microphones. A tourmaline-crystal source, calibrated by application of the principle of reciprocity, will be the

primary standard. A condenser microphone will serve as a secondary-standard source, which will be calibrated from time to time by the primary tourmaline standard.

There are common crystalline household substances which are piezoelectric under hydrostatic pressure, and which might be used as sound sources. Such are sucrose (cane sugar) and tartaric acid (sour salt). The latter at room temperatures has a piezoelectric modulus about double that of tourmaline.

The theoretical conclusions and experimental results contained in this article were reported at the meeting of the Acoustical Society of America in Washington, D. C., in April 1940. Similar theoretical conclusions were reached by W. R. MacLean [8] and published in the July 1940 issue of the Journal of the Acoustical Society of America.

I thank Elias Klein, of the Naval Research Laboratory, for securing loans of tourmaline and equipment, and for his kind help and encouraging suggestions.

VI. REFERENCES

[1] W. Voigt, *Lehrbuch der Kristallphysik* (B. G. Teubner, Leipzig, 1910).
[2] Rayleigh, *The Theory of Sound* (Macmillan & Co., London, 1896).
[3] S. Ballantine, Proc. Inst. Radio Engrs. **17,** 929 (1929).
[4] H. Osterberg and J. W. Cookson, Rev. Sci. Instr. **6,** 347 (1935).
[5] S. Ballantine, J. Acous. Soc. Am. **3,** 319 (1932).
[6] L. J. Sivian, Bell System Tech. J. **10,** 96 (1931).
[7] D. A. Keys, Phil. Mag. [6] **46,** 999 (1923).
[8] W. R. MacLean, J. Acous. Soc. Am. **12,** 140 (1940).

WASHINGTON, August 14, 1940.

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RESEARCH PAPER RP1342

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RECOMBINATION AND ELECTRON ATTACHMENT IN THE *F* LAYERS OF THE IONOSPHERE

By Fred L. Mohler

ABSTRACT

Observational data for the ionosphere at Washington have been used as a basis for computations. The rate of recombination at night is roughly proportional to the square of the electron concentration, but the apparent recombination coefficient, α', tends to increase with decreasing electron concentration over the half period of a sunspot cycle. This fact and the observed variation of α' with height indicate that electrons disappear both by recombination and by negative-ion formation. The daily variation of electron concentration indicates that the F_2 level is far above the level where the rate of production of electrons is a maximum in midsummer and that the F_1 layer is near the level where the rate is a maximum. It is assumed that both layers come from the ionization of atomic oxygen.

If α' is a function of the pressure, there will be a maximum electron concentration at a pressure, p, given by the relation

$$\frac{p}{p_0}=\frac{\alpha}{\alpha'}f(\lambda),$$

where p_0 is the pressure at the F_1 level, α is the electronic-recombination coefficient, and λ is the ratio of negative ions to electrons. $f(\lambda)$ is 1, if λ is small, or a linear function of p. In midsummer, p is 4×10^{-3} mm of mercury. $p/p_0=0.027$ and $\alpha=2\times10^{-12}$, in good agreement with the theory of recombination. A seasonal variation of p/p_0 can be explained, if $f(\lambda)$ is not always unity, as λ is very sensitive to temperature. The seasonal variation in electron concentration can be accounted for by the change in pressure. The pressure variation also accounts for the fact that F_2 changes much more than F_1 over a sunspot cycle. The effective collision area for electron attachment to oxygen atoms is 6.5×10^{-21} cm^2.

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I. INTRODUCTION

Phenomena of the ionosphere have been the subject of many theoretical investigations. The conventional theory is that electrons are produced by photoionization by solar radiation and disappear by recombination at a rate proportional to the square of the electron concentration. The different layers of ionization are usually ascribed to different absorption processes. This theory gives a very satisfactory explanation of the daily and annual variations of the E and F_1

layers,[1,2] but the F_2 layer varies in an apparently erratic manner that has never been adequately explained. This layer is characterized by a very slow rate of recombination, and Bradbury[3] has suggested that the F_2 maximum in electron concentration may come from the same ionization process that gives F_1 purely as a consequence of the slow recombination. Recombination in the ionosphere probably involves both spontaneous recombination of electrons and positive ions and negative-ion formation followed by ionic recombination, and the relative importance of the latter process will increase with increasing pressure. This paper reports an attempt to deduce the nature of the recombination processes from observational data on the F region.

II. OBSERVATIONAL DATA

Ionosphere characteristics are commonly published as plots of the critical radio penetration frequency and minimum virtual height

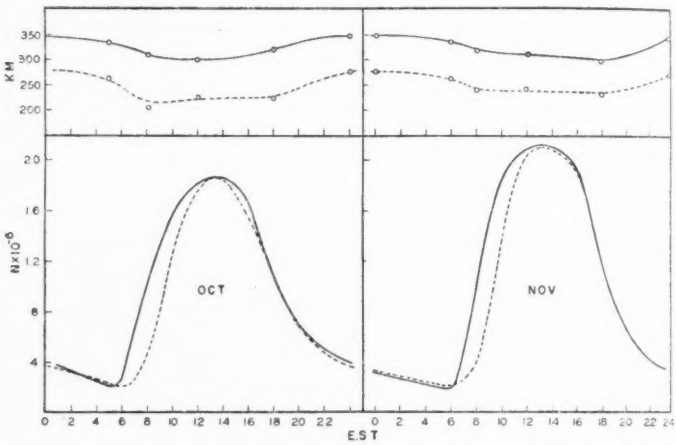

FIGURE 1.—*Mean values of electron concentration and true height of the F_2 layer for Washington, October and November 1938.*

Above, the full line is true height of the maximum, and the broken line is the height where N_e is half the maximum value. Below, the broken line is the theoretical curve for the conventional theory with $\alpha'=0.8\times10^{-10}$ in October and 1.0×10^{-10} in November.

versus the time of day. Monthly mean values for several stations are published periodically.[4] The critical frequency depends on the number of free electrons per cubic centimeter, N_e, which is here computed by the equation

$$N_e=0.0124f^2, \tag{1}$$

where f is the critical frequency in kilocycles for the ordinary wave. The question as to the proper coefficient in eq 1 is not important for this work.

The true height is not simply related to the virtual height, but methods[5] are now available for the computation of true height, and

[1] E. V. Appleton, Proc. Roy. Soc. (London) [A] **162**, 451 (1937).
[2] E. O. Hulbert, Phys. Rev. **55**, 639 (1939).
[3] Ter. Mag. and Atmos. Elec. **43**, 55 (1938).
[4] National Bureau of Standards data for Washington, D. C., by Gilliland, Smith, and Kirby, appear monthly in the Proceedings of the Institute of Radio Engineers.
[5] F. H. Murray and J. B. Hoag, Phys. Rev. **51**, 333 (1937).

N. Smith has made rather extensive computations of true heights as a function of frequency for the ionosphere at Washington during the past few years, and I am indebted to him for the opportunity to use some of this unpublished material.

A few months in 1938 have been selected as a basis for computations. Figures 1 and 2 give the number of electrons and true height as a function of the time of day for different months. This is for a period of maximum solar activity. In years of minimum solar activity the number of electrons in the F_2 layer was about one-fourth of the 1938 value, the daily curve broader and flatter.

Figure 3 is a plot of the vertical distribution of electrons above the E layer, as computed by Smith. The F_1 layer does not appear in October 1938 but is found in years of low solar activity.

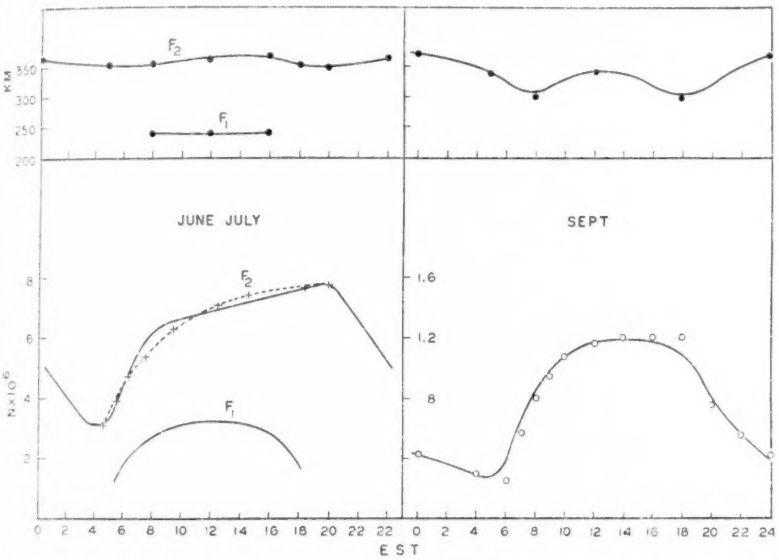

FIGURE 2.—*Mean values of electron concentration and true height for Washington, June, July, and September 1938.*

Above, true height of the maxima (F_1 is not well defined in September); below, full lines give observed values of N, (two scales). The broken line and crosses are computed on the assumption that absorption is negligible and electrons disappear purely by electron attachment; circles, on the assumption of pure recombination with no absorption.

III. ELEMENTARY THEORY

If a is the atomic-absorption coefficient of the ionizing radiation, then the flux, J, of ionizing quanta per square centimeter per second is

$$J=J_0e^{-Na},$$

where J_0 is the flux outside the atmosphere and N is the number of atoms in a square-centimeter column extending from the point where J is evaluated to the outside of the atmosphere.

The radiation is reduced to $1/e$ in a column of gas containing $1/a$ atoms per square centimeter and weighing M/a grams, where M is the weight of one atom. For vertical sunlight, M/a is the partial

pressure in grams per square centimeter, and $M/1.35a$ is the partial pressure in millimeters of mercury at the level where the radiation is reduced to $1/e$. The number of atoms per cubic centimeter at this pressure is $0.725\times10^{19}\ M/aT$, and the rate of production of electrons per cubic centimeter per second is

$$q=\frac{0.725\times10^{19}MJ_0}{T}e^{-1}, \tag{2}$$

and for any partial pressure, p,

$$q=\frac{0.725\times10^{19}MJ_0}{T}\frac{p}{p_1}e^{-\frac{p}{p_1}}, \tag{3}$$

where $p_1=M/1.35a$. If the rate of production of electrons is in equilibrium with the rate of recombination and the number of electrons per cubic centimeter, N_e, is assumed equal to the number of positive ions,

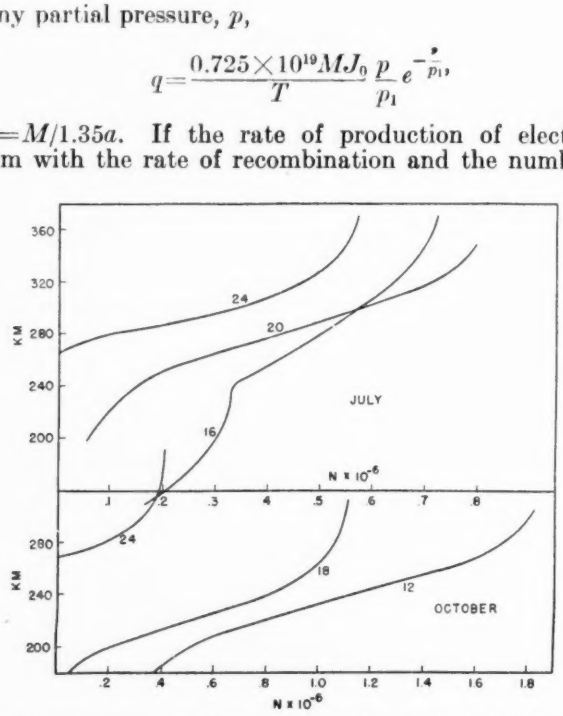

FIGURE 3.—*Electron concentration as a function of the height for Washington, July and October 1938 at the hours indicated on the curves.*

From calculations by N. Smith.

$$q=\alpha N_e^2 \tag{4}$$

$$\left.\begin{aligned} N_e&=\frac{K^{1/2}}{\alpha^{1/2}}\frac{p^{1/2}}{p_1^{1/2}}e^{-\frac{p}{2p_1}}\\ K&=0.725\times10^{19}MJ_0/T \end{aligned}\right\}. \tag{5}$$

For the case of oblique sunlight entering the atmosphere at a zenith angle, Z, the light is reduced to $1/e$ at a pressure $p_1\cos Z$, and the maximum rate of production of ions is reduced by the factor $\cos Z$.

In an atmosphere of atoms of mass, M, the relation between pressure, p, and altitude, h, can be expressed

$$\left.\begin{aligned} \frac{p_1}{p_2} &= e^{(h_2-h_1)/H} \\ H &= kT\times 10^{-5}Mg \end{aligned}\right\}, \tag{6}$$

where k is Boltzman's constant, g is the gravitational constant, and H is the height, in kilometers, in which the pressure is reduced to $1/e$ (commonly called the scale height).

It will be assumed in numerical computations that atomic oxygen gives rise to F-layer ionization. Wulf and Deming [6] have shown that the dissociation of oxygen must be nearly complete above 100 km and estimate the number of oxygen atoms per cubic centimeter at 100 km as 10^{12}. The dissociation of oxygen produces a sharply defined transition both in chemical composition and temperature near the 100-km level. If it is assumed that gases are in separate gravitational equilibrium above 100 km, then for atomic oxygen

$$H = T/18.8. \tag{7}$$

The theoretical value of the atomic absorption coefficient of oxygen [7] at the photoelectric threshold, 910 A, is 1.25×10^{-17}, and p_1 for vertical sunlight is 1.56×10^{-6} mm.

It is generally considered that at the F_1 level there will be a large proportion of atomic oxygen negative ions, and ionic recombination may be important. The rate of absorption, q, gives the rate of production of positive ions, and if λ is the ratio of negative ions to electrons,

$$N_+ = N_e + N_- = (1+\lambda)N_e, \tag{8}$$

and for equilibrium between production of ions and recombination

$$\begin{aligned} q &= \alpha N_e N_+ + \alpha_i N_- N_+ \\ q &= [(1+\lambda)\alpha + \lambda(1+\lambda)\alpha_i]N_e^2 = \alpha' N_e^2, \end{aligned} \tag{9}$$

where α_i is the ionic recombination coefficient and α' the apparent coefficient for recombination. Appleton and Sayers [8] emphasize that since the daily and annual variation of the F_1 layer conforms to the simple recombination theory, α' must be a constant and λ must be independent of pressure at the F_1 level.

The rate of recombination in the F_2 layer is very much less than in the F_1 layer, so it is necessary to assume that λ decreases with the pressure above F_1. It commonly has been assumed that spontaneous recombination of electrons and positive ions will be predominant in the F_2 layer, because the pressure is very low. However, in contrast to the F_1 layer, the daily and annual variations of F_2 ionization give no evidence that α' is independent of pressure at this height.

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[6] Ter. Mag. and Atmos. Elec. **43**, 283 (1938).
[7] D. R. Bates, R. A. Buckingham, H. S. W. Massey, and J. J. Unwin, Proc. Roy. Soc. (London) [A] **170**, 322 (1939).
[8] Union, Rad. Sci. Int. Proc., p. 272 (1938).

IV. RECOMBINATION AND ELECTRON ATTACHMENT

If electrons disappear by simple recombination during the night, then

$$\frac{dN_e}{dt} = -\alpha' N_e^2, \tag{10}$$

and the integral of this

$$\frac{1}{N_2} - \frac{1}{N_1} = \alpha'(t_2 - t_1), \tag{11}$$

where N_1 and N_2 are the number of electrons at times t_1 and t_2. Figure 4 gives plots of $1/N_e$ versus t for the data of figures 1 and 2. The

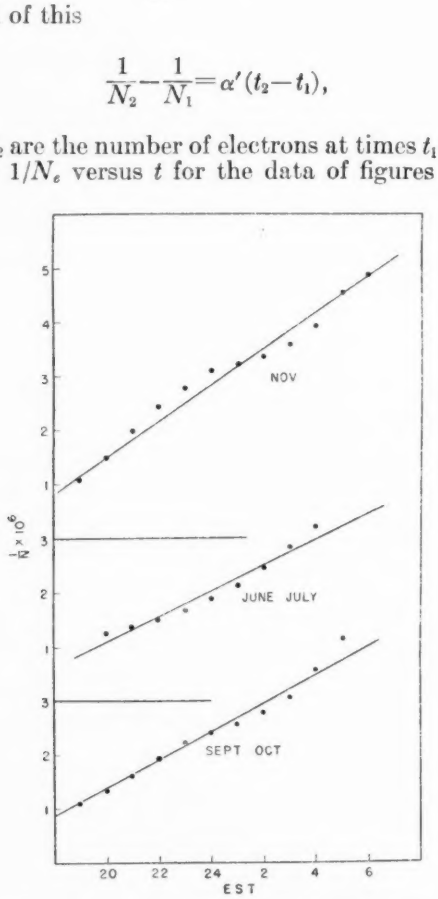

FIGURE 4.—*Plots of $1/N_e$ versus time from data of figures 1 and 2.*
Slopes of the lines give $\alpha' = 0.95 \times 10^{-10}$, 0.66×10^{-10}, and 0.72×10^{-10}, from top to bottom.

slopes of the straight lines give values of α', ranging from 0.66×10^{-10} to 0.95×10^{-10}.

Appleton [9] has pointed out that the rate of recombination during the daytime can be evaluated from pairs of values of N_e and of dN_e/dt at equal intervals before and after noon by the equation,

$$\left(\frac{dN_e}{dt}\right)_{a.m.} - \left(\frac{dN_e}{dt}\right)_{p.m.} = [(N_e^2)_{p.m.} - (N_e^2)_{a.m.}]\alpha', \tag{12}$$

[9] Proc. Roy. Soc. (London) [A] **162**, 451 (1937).

where subscripts a. m. and p. m. denote values at equal time intervals before and after noon. The October curve (fig. 1) gives a mean value of $\alpha' = 0.9 \times 10^{-10} \pm 0.2 \times 10^{-10}$, as compared with the nighttime value of 0.7×10^{-10}. Values based on sunrise and sunset values of the slopes and ordinates for 20 months in the period 1937–39 give $\alpha' = 0.9 \times 10^{-10} \pm 0.3 \times 10^{-10}$ and in the same period the mean nighttime value is about 0.7×10^{-10}. However, nighttime values for years of low solar activity (1934 and 1935) are very much larger than this, and the values of α' seem to be definitely correlated with the amount of ionization. Figure 5 is a plot of α' versus midnight values of $1/N_e$ for 30 months in the period 1934–39. Although the points are widely scattered, the plot indicates that α' is inversely proportional to N_e. This would suggest that electrons disappear by attachment rather

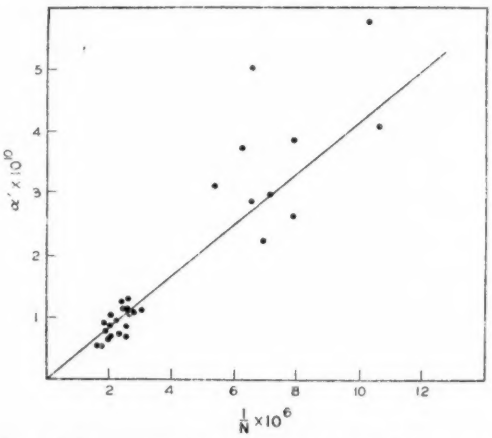

FIGURE 5.—*Values of the apparent recombination coefficient as a function of $1/N_e$ at midnight for years 1934 to 1939.*

than recombination. The time variation of electron concentration during the night would be

$$\frac{dN_e}{dt} = -\beta N_o N_e = -BpN_e, \tag{13}$$

where N_o is the number of oxygen atoms per cubic centimeter; p, the partial pressure of oxygen atoms; β and B, constants. The integral of this is

$$\ln N_1 - \ln N_2 = Bp(t_2 - t_1). \tag{14}$$

Values for midnight and 4 a. m. for the 30 months considered above give values of Bp which are far from constant but show no systematic variation with N_e. The mean value is $Bp = 2.9 \pm 0.8 \times 10^{-5}$.

It seems impossible to admit, however, that electrons disappear purely by electron attachment, for this would not give a well-defined maximum in the vertical distribution of electrons, such as is observed, but rather a gradual exponential variation proportional to e^{-p}. It is of interest to investigate the possibility that electrons disappear

both by recombination and attachment. Then the nighttime variation would be

$$-\frac{dN_e}{dt}=\alpha N_e N_+ + BpN_e, \tag{15}$$

and, by eq 8,

$$-\frac{dN_e}{dt}=\left[\alpha(1+\lambda)+\frac{Bp}{N_e}\right]N_e^2, \tag{16}$$

where λ is as before the ratio of negative ions to electrons.

The consequences of such a law are complicated, for the expression in brackets can be treated as a recombination coefficient which depends upon the electron concentration, the pressure, and possibly on the temperature, since λ may be very sensitive to temperature. This will make the apparent value of the recombination vary with the solar activity, the season, and the time of day, but the rate of change in ionization may be roughly proportional to N^2_e, as is found to be the case.

The nighttime variation of N_e for June and July (fig. 2) can be represented by the equation

$$-\frac{dN_e}{dt}=0.3\times10^{-10}N_e^2+2\times10^{-5}N_e. \tag{17}$$

This applies to a level of mean height, 360 km. The data of figure 3 permit an evaluation of dN_e/dt at lower levels, and indicate a value of $Bp=17\times10^{-5}$ at 270 km, assuming pure electron attachment. Taking the scale height as 36 km, the pressure at 270 km is 12 times the pressure at 360 km and the attachment coefficient 8.5 times as great.

The pressure variation of electron attachment tends to make the F layer rise during the night, and this is almost always observed from sunset to midnight. This pressure change complicates the problem of determining the rate of recombination and attachment. From midnight to dawn the height decreases slightly, and this is naturally ascribed to cooling of the air. However, the temperature changes introduce a further source of uncertainty in the computations. While curves of the type of figure 3 should give specific information as to the rate of recombination as a function of altitude, real or accidental variations make it impractical to evaluate the constants involved in eq 16.

V. DAYTIME VARIATION OF ELECTRON CONCENTRATION

The daily variation of N_e, on the basis of the simple recombination theory, has been evaluated by Millington [10] for conditions comparable to October and November 1938. The broken-line curves in figure 1 show these theoretical curves, and, except for a large discrepancy in the morning, the daily variation corresponds roughly to theory. The daily curves for September, June, and July rise more abruptly at sunrise, and the maximum is near sunset. The shape of the curves suggests that the ionizing radiation is not reduced appreciably by atmospheric absorption and that the F_2 level is far above the level

[10] Proc. Phys. Soc. (London) **44**, 580 (1932).

where the radiation is reduced to $1/e$. On the assumption that the F_2 level is at a constant pressure so low that absorption is negligible and that electrons disappear by attachment,

$$\frac{dN_e}{dt}=q-BpN_e=BpN_\infty-BpN_e, \tag{18}$$

where q is a constant from sunrise to sunset, and N_∞ is the equilibrium number of electrons reached after a sufficiently long time. The integral of this between times t_1 and t_2 is

$$Bp(t_2-t_1)=\ln\left(\frac{N_\infty-N_1}{N_\infty-N_2}\right). \tag{19}$$

Figure 2 includes a plot of this equation for June and July, taking N_1 as the observed value at dawn, $Bp=6\times10^{-3}$ and $N_\infty=0.8\times10^6$. The agreement is satisfactory, but it happens that the assumption of pure recombination gives a very similar curve. On the September curve of figure 2 the circles are computed on the assumption of pure recombination with no absorption, using the constants $\alpha'=0.7\times10^{-10}$ and $N_\infty=1.2\times10^6$. The curves clearly indicate that the atmospheric absorption is negligible, but they do not give conclusive evidence as to the law of recombination. The surprising conclusion is, that in the summer the F_2 layer is far above the level where radiation is reduced to $1/e$, while in the winter it is much closer to that level. From curves of Chapman [11] for ion production at different heights, it is estimated that if absorption is negligible within an hour of sunrise, then the F_2 level is more than 3 times the scale height, or over 100 km above the level where radiation is reduced to $1/e$. This rough estimate supports Bradbury's suggestion that F_1 and F_2 come from the same ionization process with the maximum rate of production of ions at the F_1 level.

VI. PRESSURE AT THE F_2 LEVEL

It is convenient to determine the pressure at which N_e is a maximum rather than the height. For midday conditions the number of electrons as a function of pressure can be expressed.

$$\alpha' N_e^2=\frac{Kp}{p_o}e^{-p/p_0} \tag{20}$$

$$\alpha'=\alpha(1+\lambda)+\frac{Bp}{N_e}, \tag{21}$$

where p_0 is the pressure at the level where radiation is reduced to $1/e$. As a simple working hypothesis, assume that λ is proportional to p ($\lambda=cp$). The condition that there be a maximum value of N_e at a pressure p is that $N_e^2 d\alpha'/dp$ is equal to the derivative of the right side of eq 20, N_e being taken as a constant.

$$\left(\alpha c+\frac{B}{N_e}\right)N_e^2=\frac{Ke^{-p/p_0}}{p_0}\left(1-\frac{p}{p_0}\right) \tag{22}$$

$$\alpha cp+\frac{Bp}{N_e}=\alpha'\left(1-\frac{p}{p_0}\right)$$

[11] Proc. Phys. Soc. (London) **43**, 26 (1931).

$$\frac{p}{p_0}=\frac{\alpha}{\alpha'}, \tag{23}$$

where p is the pressure at the F_2 maximum, and p_0 is the pressure at the level where the radiation is reduced to $1/e$. This would indicate that if the F_2 level is far above p_0, then the effective recombination coefficient, α', is much greater than the electronic recombination coefficient. However, the large seasonal change of p/p_0 is not explained, for observed variations of α' are in the wrong direction. In general, if λ is not a linear function, p/p_0 will be a function of λ and, as λ is very sensitive to temperature, a seasonal variation can be understood. A physically simple assumption is that formation of negative ions by attachment and disappearance by recombination are in equilibrium.

$$\lambda(1+\lambda)\alpha_i N_e^2=BpN_e \tag{24}$$

$$\frac{d\lambda}{dp}=\frac{B}{(1+2\lambda)\alpha_i Ne} \tag{25}$$

The substitution of this value of $d\lambda/dp$ in place of c in eq 22 gives, instead of eq 23, the relation

$$\frac{p}{p_0}=\frac{(1+\lambda)^2\alpha}{(1+2\lambda)\alpha'} \tag{26}$$

If λ is small (1 or less), eq 26 is nearly identical to eq 23, but, in contrast to eq 23, a seasonal variation in p/p_0 can here be ascribed to λ. There is no reason to believe that either equation is rigorous, but the derivations at least show, in a qualitative way, that there can be a maximum value of N_e far above p_0. It is not true, as has been suggested, [12] that electronic recombination is predominant at this maximum, but, on the contrary, it must be a small fraction of the apparent recombination coefficient, α', if p/p_0 is very small. It seems probable that the vertical variations of λ and $d\lambda/dp$ are subject to random variations and cannot be expressed as simple analytical functions. This would explain the large fluctuations in N_e and in the height of F_2, which are commonly but not always observed. However, Appleton's assumption that λ reaches a constant value at the F_1 level must be preserved for the reasons which he has given.

VII. NUMERICAL RESULTS

It will be assumed, following Bradbury's suggestion, that p_0 is at the F_1 level and that the ionization comes from atomic oxygen. Then the partial pressure for June and July noon is 1.48×10^{-6} mm at 240 km and (from section III) the effective temperature between 100 and 240 km is 680°K; the scale height, 36 km. This scale height will be used above 240 km for want of further data. In June and July the F_2 level is at 360 km, $p/p_0=0.027$, and $p=4\times10^{-8}$ mm Hg. If it is assumed that λ is 1 or less, eq 23 is a good approximation, and on the basis $\alpha'=0.8\times10^{-10}$, it follows that α, the coefficient of electronic recombination, is 2×10^{-12} (eq 26 indicates that α may be less).

[12] N. E. Bradbury, Ter. Mag. and Atmos. Elec. 43, 55 (1938).

A recent theoretical computation [13] of the recombination coefficient for atomic oxygen gives almost exactly this value; namely, 2.12×10^{-12} at 500°K. It would appear then that in this case λ must be small, and in the expression for α' electron attachment must be predominant. For October p/p_0 is larger and λ is evidently not negligible.

The measured rate of production of ions at the F_2 level for June and July is 47 per cubic centimeter per second. It follows from the above values of $p_{\frac{1}{m}}$ and p_0 in eq 3 that the rate of production at $F_1(p=p_0)$ is 640 per cm^3 per sec. This and the observed value of N_e give $\alpha'=5\times10^{-9}$ at F_1. An independent estimate of α' at F_1 can be made with the approximation that electron attachment is predominant. The value $Bp=6\times10^{-5}$ at $F_2(p=4\times10^{-8}\,\text{mm})$ gives $\alpha'=Bp/N_e=6.2\times10^{-9}$ at $p=1.48\times10^{-6}$ mm, in good agreement with the first value.

The outstanding anomaly of the F_2 layer has been the seasonal variation of N_e, but this can be entirely accounted for by the seasonal variation in pressure. The maximum rate of production of ions, $\alpha' N^2_e$, for October is 5.8 times the rate for July instead of 0.7 times the July value, as predicted by conventional theory. Since this rate is proportional to p exp. $(-p/p_0)$, then the pressure at F_2 is 7.3 times the July value. The observed difference in height is 70 km, and if the scale height is 36 km, this would correspond to a pressure ratio of 7.0.

While this pressure variation has been ascribed to a seasonal variation in λ, there is no basis for quantitative predictions. For temperature equilibrium between oxygen atoms, electrons, and ions, the ratio of ions to electrons would be given by Saha's equation with the electron affinity, 2.2 volts, in place of the ionization potential.

$$\frac{N_e N_0}{N_-}=\frac{N_0}{\lambda}=6.05\times10^{15}T^{3/2}e^{-2.2\times11600/T}, \tag{27}$$

where N_0 is the number of oxygen atoms per cubic centimeter. At a partial pressure of 4×10^{-8} mm, λ would become unity at 960° K, and at this temperature a 10-percent change in T would give a tenfold change in λ. Oxygen ions exposed to sunlight cannot be considered to be in temperature equilibrium, and λ is probably much less than the value given by eq 27. The assumptions that λ is 1 or less at a pressure of 4×10^{-8} mm, and larger but variable at 7 times this pressure, are not incompatible with eq 27 though there is no good basis for numerical computations.

VIII. CONCLUSION

To summarize the results there is little doubt that the rate of recombination decreases rapidly with decreasing pressure above F_1 and a necessary consequence of this is that the maximum number of electrons is far above the level where the rate of production is a maximum. The analysis given here involves simplifying assumptions that may well be open to question, but several independent lines of evidence indicate that the maximum rate of production must be near the F_1 level so that one absorption process can account for both

[13] D. R. Bates, R. A. Buckingham, H. S. W. Massey, and J. J. Unwin, Proc. Roy. Soc. (London) [A] **170**, 322 (1939).

F layers. This avoids the assumption that the temperature above F_1 is extremely high and subject to enormous seasonal variations. A complication in the theory is that the height of F_2 and the electron concentration depend on the ratio of electrons to negative ions, which is extremely sensitive to temperature. Small changes in the vertical temperature gradient could produce large fluctuations in the F_2 layer, and it is possible that this can explain the apparently erratic variations in ionization that are characteristic of the F_2 layer.

One consequence of the theory is, that the variation of ionization with time and height will depend on the absolute intensity of the ionizing radiation, which varies over a wide range during a sunspot cycle. In periods of low solar activity, with low values of N_e, the electron attachment becomes relatively more important, the maximum rises to a lower pressure, and even in winter the F_1 layer appears as a separate maximum. N_e for the F_1 layer should vary as the square root of the intensity of the ionizing radiation. In the F_2 layer the relation between N_e and intensity is more complicated, but for summer conditions (electron attachment predominant) it will vary nearly as the first power of the intensity.[14] From July 1934 to July 1938 the F_1 ionizatoin increased by the factor 1.54, the F_2 ionization by the factor 2.34, which is almost exactly the square of 1.54.

The values of $Bp=6\times10^{-5}$ at $p=4\times10^{-8}$ mm and $T=680°$ K lead to a value of the effective collision area, σ, for electron attachment to atomic oxygen of 6.5×10^{-21} cm^2. Massey [15] has published a rough theoretical estimate for this constant of 2.5×10^{-22} cm^2 at 680° K. This agreement is poor, but both values are subject to considerable uncertainty. As noted above, the computed value of the electronic recombination coefficient, 2×10^{-12}, is in accurate agreement with theory, though the uncertainty in this case also is large. The effective collision area for recombination at 680° K is 1.2×10^{-19} cm^2.

The author [16] measured the rate of recombination in low-pressure cesium and mercury discharges and obtained values of $\alpha=2$ or 3×10^{-10}. Doubt was expressed as to whether this was the coefficient for spontaneous recombination, but the fact that α' for the F_2 layer is of the same magnitude has been quoted as evidence that α' was the electronic recombination coefficient. This is evidently not the case, and the ionosphere results seem to be consistent with the recombination theory.

WASHINGTON, June 8, 1940.

[14] In a previous publication the author has considered that N^2, was a measure of the ionizing intensity both for F_1 and F_2, but this is inconsistent with the present theory. See Science **90**, 137 (1939).
[15] Proc. Roy. Soc. (London) [A] **163**, 542 (1937).
[16] J. Research NBS **19**, 447 (1937) RP1037; **19**, 559 (1937), RP1045. There is a numerical error in the theoretical value of α used in the second paper.

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COMBINATION OF WOOL PROTEIN WITH ACID AND BASE: THE EFFECT OF TEMPERATURE ON THE TITRATION CURVE

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ABSTRACT

Equilibrium measurements are reported of the amounts of hydrochloric acid and potassium hydroxide bound by wool, as a function of pH and salt concentration at 0°, 25°, and 50° C. In order to eliminate from the measurements of base combination effects due to decomposition, a study was also made of the effect of temperature on the rate of decomposition of the disulfide bonds in wool and on the rate of solution of the fiber in alkaline solutions. The data support the assumption made in accounting for previously reported titration measurements at 0° C, that the carboxyl and amino groups of wool in the uncombined state are completely ionized. Thus changes in the pH coordinates of the titration curves brought about by changes in temperature are small in the pH range in which acid is combined, which indicates that combination with acid is equivalent to back-titration of the carboxyl groups, but are large in the pH range in which base is combined, which indicates that combination with base is equivalent to back-titration of amino groups.

The heats of dissociation calculated for the two kinds of groups, approximately 2,500 and 14,000 calories, respectively, are in good agreement with values for these groups in comparable compounds and in soluble proteins. The value obtained in the acid range also agrees with the results of calorimetric measurements on the combination of acid with wool.

It is shown that approximately equal parts of the total heat changes in the acid range are associated with the dissociation of hydrogen ions and chloride ions from the fiber. An appreciable part of the total heat effect may be ascribed to a heat of transfer of the ions between the two phases of the heterogeneous titration system. Neither titrimetric nor calorimetric estimations of the heats of dissociation provide evidence for or against the existence of "salt linkages" in wool.

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I. INTRODUCTION

Measurements of the dependence on pH and salt concentration of the amounts of hydrochloric acid and potassium hydroxide bound by wool at 0° C. have been described in an earlier publication by two of the present authors [29].[2] The proposed theoretical analysis of these measurements was based on the assumptions: (1) That in the uncombined state the carboxyl groups and basic groups are completely ionized, i. e., the hydrogen atoms of the carboxyl groups have been transferred, with their positive charges, to the amino and guanidino groups, leaving negatively charged carboxylate groups and positively charged alkylammonium groups; (2) that when the protein combines with hydrogen ions it also forms partially dissociated stoichiometric complexes with negative ions, (e. g., Cl^-), and when it combines with hydroxyl ions, it forms similar complexes with positive ions (e. g., K^+). The first assumption is equivalent to postulating for the protein the same zwitterion [3] structure originally proposed for amino-acids and certain other ampholytes by Adams [1] and by Bjerrum [2], and now almost universally adopted as the result of the researches of Bjerrum [2], Harris and Birch [15], Wyman [35], Cohn and his collaborators [7], and others. The purpose of the present paper is to adduce evidence justifying application of the dipolar ion concept to wool protein. Experiments designed to further justify and extend the second and less familiar assumption are at present in preparation for publication.

It was pointed out by Bjerrum that the effects of temperature on the dissociation constants of the α-amino-acids furnished an indication of their existence as dipolar ions. Since the publication of Bjerrum's paper this criterion has been made use of in the study of proteins as well as of amino-acids by Pertzoff and Carpenter (casein) [24], and by Wyman (hemoglobin) [36]. Changes in temperature were observed to have very small effects on the parts of the titration curves of these proteins which lie on the acid side of neutrality, but the effects on the alkaline side were very considerable. These results may be understood if these proteins are, like their constituent amino-acids, dipolar ions, since then the addition of alkali to their solutions serves mainly to remove hydrogen ions from amino groups, the dissociation constants of which are very dependent upon temperature.

Measurements of the effects of temperature on the titration curves of wool keratin, presented in the present paper, lead to the same conclusion. They also offer a means of evaluating the energy changes accompanying the associations of anions and cations, postulated in assumption 2. It is a consequence of this assumption that the anions of different acids should be characterized by different affinities for wool (i. e., this affinity is inversely related to the degree to which they dissociate under standard conditions).[4] The existence of these postulated differences in affinity would be manifested by different positions with respect to the pH coordinates of the titration curves of wool obtained with different acids.[5] The differences in affinity, if sufficiently large, would be accompanied by varying degrees of sensitivity

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] In the remainder of this paper the term "dipolar ion" is substituted for "zwitterion" in conformity with recent American usage [6, 7].

[4] It has been demonstrated [28, 30] that very wide differences do indeed exist between the affinities of the anions of various acids for wool and for other proteins.

[5] In the case of acid dyes this affinity is directly related to fastness to washing and to alkalies.

of the respective titration curves to changes in temperature. While an inverse relation between the magnitudes of dissociation constants and the heats of the corresponding dissociations is not regular or exact, it is so general that the demonstration of an increased temperature dependence of the titration curve with ions of high affinity should be an essential part of the experimental validation of the second assumption. Because of the wide use of hydrochloric acid by all investigators of the acidic and basic properties of wool as well as of other proteins, and because the data with this acid are unusually complete, it is convenient to refer all comparisons of the titration curves of wool with other acids to the common basis of its titration curve with hydrochloric acid, and to express the affinities of the anions of other acids in terms of the affinity of wool for chloride ions. For this purpose one needs not only titration data with hydrochloric acid at a single temperature, such as have already been described [29], but also measurements of the effect of temperature on the same equilibrium, as given in the present paper. In order to obtain accurate data in solutions of alkaline pH, at which decomposition of the disulfide bonds occurs very rapidly at room temperature, it has also been necessary to investigate the lability of this bond as a function of temperature as well as of pH and concentration of ions.

Irrespective of what views may be entertained as to the nature of the equilibria involved in the titration of wool with acid or base, it is desirable to appraise any effect which may be produced on the normal temperature dependence of a protein titration curve by the circumstance that the titration system exists in two phases. With this information at hand, it should be possible to determine the relationship of the detailed titration measurements previously obtained at 0° C to the phenomena of combination of acid and base by wool at the elevated temperatures which prevail when wool is exposed to acid or base during carbonizing, acid-dyeing, scouring, and milling. If an effort is to be made to relate the equilibria in such a process as acid-dyeing to the acid-base equilibrium between wool and an inorganic acid, the latter must be defined at the temperature at which the process in question is normally carried out.

II. EXPERIMENTAL PROCEDURE

Details of the preparation of materials and of most of the methods used in the present investigation have already been described [29]. Modifications in the procedures, or considerations bearing on their applicability to measurements made at high temperatures, are listed in the following sections:

1. MATERIALS

In order to assure that data obtained at different temperatures might be legitimately compared, most of the measurements were made on a single large batch of root wool fibers, purified as previously described [29] and carefully mixed before the final carding to insure homogeneity. Thus, certain of the measurements previously made at 0° C with a different batch of wool have been repeated, and use has been made of the earlier measurements at this temperature only in certain cases in which a number of duplicate measurements with the new batch of wool showed the essential identity of the two sets of

results. On incineration at 700° C the wool used left an ash of 0.26 percent; the hydrogen-ion equivalence of its cation content, as shown by electrodialysis [26], was 0.036 millimole per g. Measurements of the amounts of acid or base bound have been corrected for the alkali equivalence of the ash by subtracting from or adding to the measured acid or base bound an amount, 0.032 millimole per g, determined by direct comparison with the wool containing only a negligible amount of ash used in the previous investigations [29], as well as by subtracting the average amounts of chloride removed from solution in a large number of measurements from the average amount of hydrogen ion taken up in the same series. The closeness of the empirical correction, 0.032, to the equivalence of the cationic ash, 0.036, shows that the larger part of the cations are combined with the fibers as base, and are not present as adsorbed or entrained inorganic salts. Although the amount of ash is small, and due allowance has been made for its alkali equivalence in calculating the amounts of acid or base bound by wool free of ash, it must be recognized that the presence of an alkaline ash in the fibers results in the introduction of small amounts of salt into all the acid solutions, including those to which no salt was intentionally added. Thus, curves obtained with acid in the absence of added salt may nevertheless show small effects characteristic of the presence of traces of added negative ions [29], especially in the pH region where very small amounts of acid are combined.

2. METHODS

(a) TITRATION WITH ACID

Hydrolysis of amide groups from glutamine and asparagine residues contained in the protein was considerably more rapid at 40° and 50° C than at the lower temperatures previously reported. The extent of hydrolysis was minimized by limiting the time of immersion of the wool to approximately 24 hours, an interval which proved sufficient for attainment of equilibrium at 25° C and at higher temperatures. Even in this shorter time, however, sufficient hydrolysis occurred to require the application of corrections for the ammonia produced. Thus, at 50° C, 0.5 *M* hydrochloric acid liberated approximately 0.12 millimole per g of wool per day, and 0.2 *M* acid liberated 0.035 millimole per g of wool per day. The presence of salt (potassium chloride) increased these rates. In addition to ammonia, very small amounts of other soluble products were formed at 40° and 50° C, as evidenced by the weak positive biuret test given by the solutions. With the concentrations of acid used, the biuret test was always negative in experiments at temperatures below 25° C, even after periods of immersion up to 4 or 5 days. The appearance of soluble, peptide-like decomposition products at higher temperatures is probably not accompanied by any appreciable increase in the number of basic groups in the insoluble residue, since no increase in the maximum combining power of wool for acid is found at 50° C over the value for 0° C previously reported, when corrections are properly applied for the effects of the hydrolytic production of ammonia.[6] The presence of

[6] The reported increase in the capacity of wool to bind hydrochloric acid at high temperatures [10] may be explained by the failure to take into account the production of ammonia and its effect on the titers of the aliquots used in obtaining the measurements. The causes of the effects observed by the same investigators with dye acids are undoubtedly more complex.

dissolved fragments of protein in the aliquots titrated should be without effect on measurements of the acid taken up by the protein when indicators having end points well on the acid side of neutrality are employed in the necessary titrations.

(b) TITRATION WITH BASE

Harris and Rutherford have shown [16] that when wool is exposed to alkaline solutions, disruption of its disulfide bonds results in the more or less rapid formation *in the fiber* of groups which combine with base (tentatively identified as sulfhydryl), and that the number of acid groups which are formed in this manner approaches as a limit the number of cystine residues initially present. At the same time half of the sulfur originally contained in the cystine is found in solution as inorganic sulfide. By determining the dissolved inorganic sulfide and applying additional small corrections for the wool dissolved [29] an estimate can be made of the extent of decomposition of the disulfide linkages. It is an empirical fact that at all temperatures reported in the present paper, increases in the amounts of base bound, as a function of time of exposure to alkaline solutions, closely parallel the production of dissolved sulfide. This finding, originally reported for 0° C by Harris and Rutherford, provides a basis for distinguishing between the additional base bound by acid groups, formed as the result of decomposition at any temperature, and the base that is bound by the residual unmodified protein. The application of this correction merely requires subtraction of the number of equivalents of sulfur split off per gram of wool from the total amount of base neutralized per gram in the same experiment.[7] This procedure clearly involves the assumption that the newly formed acid groups are sufficiently strong to combine *quantitatively* with base at the pH values at which disulfide break-down occurs. At 0° C and at 25° C the range of pH in which appreciable quantities of inorganic sulfide are found in solution is sufficiently high, especially when data are obtained in the absence of added salt, so that this assumption is not called into question, even when it is postulated that the groups formed are the very weakly acid sulfhydryl, formed by hydrolysis of the disulfide bonds [8, 16]. The dissociation constant at 25° C of the sulfhydryl group of cysteine itself is not far from 10^{-10} [4], and practically quantitative combination of this acidic group with base can be expected at pH values above 12. In the presence of 0.2 *M* potassium ions at 25° C little sulfur is split out within 24 hours at pH values below 12, and in the absence of added salt practically no decomposition occurs at pH values below 12.5. At lower temperatures the pH range in which decomposition occurs is even more favorable to the concept of quantitative combination with base by sulfhydryl groups having dissociation constants not far from those of the sulfhydryl in cysteine. Nothing is known of the acid strength of sulfhydryl groups in proteins, but recent work with peptides of cysteine [11] indicates that they may be expected to be stronger rather than weaker than in cysteine itself; thus the quantitative combination with base of this group in proteins at the pH values at which the decomposition of wool occurs at low temperatures is a virtual certainty.

[7] A slight modification of this correction, required when large amounts of wool are dissolved, takes account of the contribution of the dissolved wool to the total inorganic sulfide in solution [29].

At 50° C the evidence also indicates practically quantitative combination of the newly formed acid groups with base, but the lowest pH at which extensive decomposition is found at this temperature is very much lower than when low temperatures are used. In the presence of 0.5 *M* potassium ions, appreciable decomposition within 24 hours occurs at pH values only slightly higher than 8, and even in the absence of salt appreciable loss of sulfur within this time is found at pH values below 10. Unless the sulfhydryl groups which may be formed are more than one thousand times more acidic in the protein than in the amino-acid cysteine, it may not be assumed that stoichiometric combination between these groups and base would occur in this range of pH. Nevertheless, the evidence for the occurrence of such stoichiometric combination is as strong in the measurements at 50° C. as it is for the experiments at lower temperatures.

One possible alternative to attributing the necessary relatively large acid dissociation to sulfhydryl groups in the protein lies in the possibility that the newly formed acid groups may be other than sulfhydryl. Thus, for example, the sulfhydryl groups produced by the hydrolytic reaction postulated by Harris and Rutherford might be readily oxidized by air in alkaline solutions to stronger sulfur acids. No evidence at present available demonstrates conclusively the presence of appreciable quantities of free sulfhydryl in wool from which almost one-half of the initial content of sulfur, has been removed by severe treatment with alkali at temperatures between 0° and 50° C. Such wool gives little or no reaction with the nitroprusside reagent, and treatment with *p*-chlorobenzyl chloride fails to introduce significant amounts of chlorine into the fiber.[8] The present incomplete evidence may thus be interpreted as favoring the view that if sulfhydryl groups are initially formed, they are rapidly transformed to other radicals with more strongly acidic properties than those usually attributed to sulfhydryl groups in familiar compounds. Application to the titration data of the correction for the formation of new acid groups does not depend on speculation as to the nature of these groups but rests upon the experimental demonstration that such groups are actually produced. Details of this demonstration, already furnished by Harris and Rutherford in work at 0° and 22° C, have been extended to measurements made at 50° C and are indicated in part in the section that follows.

It is noteworthy that at 50° C the corrections for the protein dissolving in alkaline solutions became almost negligible because the proportion of the total wool which dissolves at a given degree of decomposition of the disulfide bonds diminishes sharply as the temperature is increased. Thus, for example, under conditions causing the splitting of 25 percent of the disulfide bonds after a day of exposure to alkali at different temperatures, it is found that approximately 3.0 percent of the fiber has dissolved at 0° C, only 1.5 percent has dissolved at 25° C, and less than 0.8 percent has dissolved at 50° C. This effect, which might appear contrary to the usual effect of temperature on solubility, is readily understood on considering the pH values at which the same given degree of decomposition of the disulfide bonds takes place in 24 hours at the three temperatures—pH 14.1 at

[8] It has been shown [23] that when sulfhydryl groups are formed by *reduction* of the disulfide groups in wool they may be quantitatively alkylated or aralkylated with alkyl or aryl halides. By using *p*-chlorobenzyl chloride as the aralkylating agent the extent of the aralkylation may be determined by subsequent analysis of the fibers for chlorine.

0° C, pH 12.4 at 25° C, and pH 9.3 at 50° C. It thus appears that the dissolving of wool in alkaline solutions does not depend solely on the combination of the newly formed acid groups with base, but that a large proportion of the preexisting groups in the fiber which undergo acidic dissociations in alkaline solutions (largely RNH_3^+ groups from lysine and arginine) must react with base before dissolution occurs. (The removal of a hydrogen ion from RNH_3^+ groups increases the net negative charge of the protein as effectively as the ionization of a carboxyl group.) This conclusion is supported by the way in which the amount of wool dissolved depends on pH at the three temperatures. At each temperature the amount dissolved per disulfide bond broken is practically constant (at the level indicated by the preceding figures) until at least one-quarter of the disulfide bonds have been disrupted. Beyond a certain pH characteristic of each temperature this constancy no longer prevails, and the amount dissolving per additional disulfide bond broken increases rapidly. At 0° C this critical pH is approximately 14, at which value between 30 and 40 percent of the cystine has been destroyed; at 25° C the rapid increase in solubility begins at about pH 13, at which value, however, over 60 percent of the cystine has broken down; at 50° C the sharp rise in solubility occurs near pH 11.6 after 80 percent of the intial content of cystine has been lost. The differences between these pH values, *which do not correspond to the decomposition of a definite proportion of the disulfide bonds in the protein,* is approximately the same as the differences between the position of the titration curves along the pH axis at the same temperatures. Since in these ranges of pH, the curve is largely determined by the equilibrium $RNH_3^+ + OH^- \rightleftharpoons RNH_2 + H_2O$, it seems probable that the dissolution of wool requires the combination with base of a large proportion of the preexisting, as well as of the newly formed acidic groups. It should thus be possible, by treating wool at elevated temperatures with solutions only slightly to the alkaline side of neutrality, to destroy practically all the disulfide bonds in its structure without dissolving an appreciable amount of the fibers.

(c) MEASUREMENT OF pH

The accuracy of the pH measurements between pH 7 and pH 10 was improved by calibrating the glass electrode with 0.05 *M* sodium tetraborate at all of the temperatures at which measurements were made, in addition to employing the other pH standards already enumerated [29]. The value, 9.180, given by Hitchcock and Taylor [17] for 25° C was used as the basis for calculating the pH values of this buffer at 50° C from the ratio of the dissociation constants of boric acid at 50° and 25° C as given by Owen [21, 22]. The same procedure was used in determining the pH value of this buffer for 0° C, but an extrapolated value of the dissociation constant was employed, since Owen's data do not extend below 5° C. The values employed in standardizing the electrode were 9.39 at 0° C, 9.18 at 25° C, 9.07 at 40° C, and 9.04 at 50° C.

By employing a standard in this range of pH, in which the glass electrode starts to deviate from the theoretical behavior of a perfect hydrogen electrode, it was possible to obtain more nearly exact correction terms for the pH measurements made in solutions above pH 9 than when the correction was averaged over the long interval between the pH of phthalate buffer and that of the dilute potassium

hydroxide solution previously described. All determinations of pH values above 5.5 were made at the temperature at which the titration curves were measured. Control measurements showed that pH measurements at room temperature could be substituted for measurements at the temperature of the experiment at pH values below 5.5.

(d) CONTROL OF TEMPERATURE

The thermostatic equipment previously described kept the temperature constant within $\pm 0.01°$ at 0° C, within $\pm 0.02°$ at 25° C, within $\pm 0.1°$ at 40° C, and within $\pm 0.5°$ at 50° C.

III. RESULTS AND DISCUSSION

Measurements of the combination of wool with both hydrochloric acid and potassium hydroxide as a function of pH were made at 0°, 25°, and 50° C. Sets of measurements were made with solutions which contained no added salt, and with solutions to which a neutral salt, potassium chloride, had been added in quantities sufficient to maintain predetermined constant concentrations of chloride ions in the experiments with acid, and constant concentrations of potassium ions in the experiments with base. Two constant ionic concentrations, 0.2 and 0.5 *M* were used. A fourth temperature, 40° C, was included among those at which measurements of combination with acid were made in the series of solutions to which no salt was added, and 25° was omitted from the temperatures at which measurements were made in solutions of 0.5 *M* ionic strength. The results obtained in the three different sets of measurements are summarized in table 1. The measurements are represented graphically in figures 1, 2, and 3, in each of which results obtained at different temperatures in a given ionic environment are directly compared. In each figure the points on the alkaline side of neutrality connected by the broken curves represent measurements of base bound, calculated in the accustomed way [29], from determinations of changes in the titer of alkaline solutions in which samples of wool have been immersed for approximately 24 hours. The points immediately above each of these, connected by the solid curves, represent the same measurements after application of the corrections for the effects of disulfide breakdown discussed in section II. The necessity of making corrections for disulfide hydrolysis when working at temperatures near 0° and 25°C has already been demonstrated [16, 29]. The present measurements show that the errors which would be introduced by neglecting to take disulfide hydrolysis into account are even more serious at 50°C than at the lower temperatures. Thus the positions of the broken curves, representing measurements made after 24 hours, are in part fortuitous and depend in a high degree on the length of time during which the wool is immersed in the experimental solutions. Points representing the corrected measurements, however, always fall on or near the appropriate solid curve, regardless of the time elapsing before the solutions are sampled, provided that sufficient time has been allowed for attainment of equilibrium. These statements are illustrated by sets of measurements, represented by crosses, made after the wool has been immersed in the experimental solutions for 3 or 4 hours in place of the longer period. The lower of each pair of two crosses at the same pH, shows the calculated amount of base

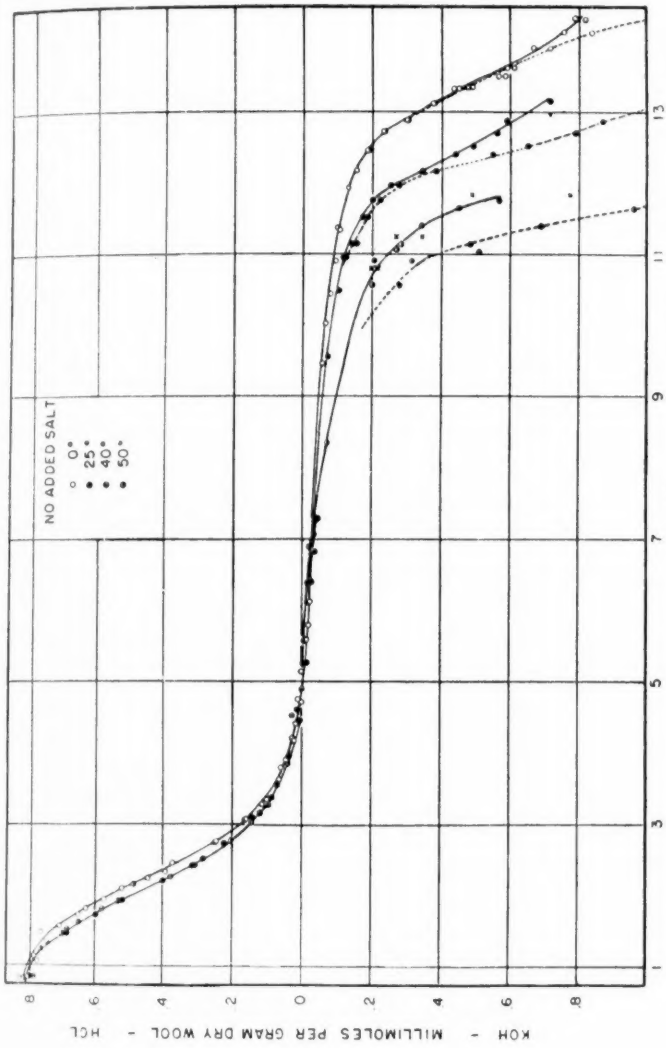

FIGURE 1.—*Combination of wool with hydrochloric acid and with potassium hydroxide as a function of* pH *and temperature, in the absence of added salt.*

The difference between the solid lines and the broken lines is explained in the text.

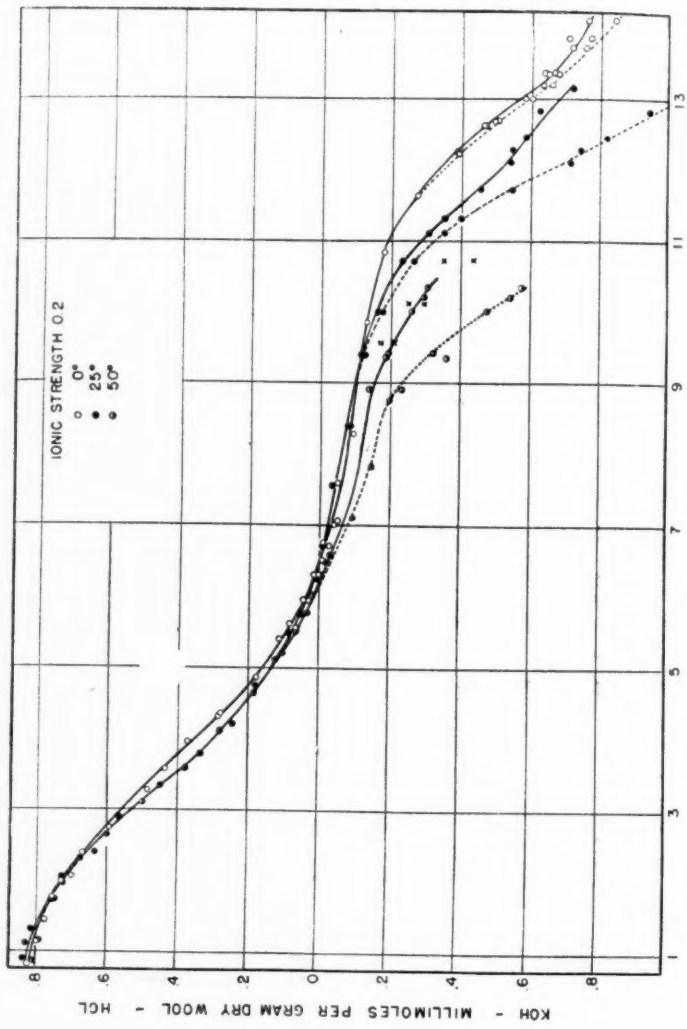

FIGURE 2.—*Combination of wool with hydrochloric acid and with potassium hydroxide as a function of pH and temperature, at 0.2 M ionic strength.*

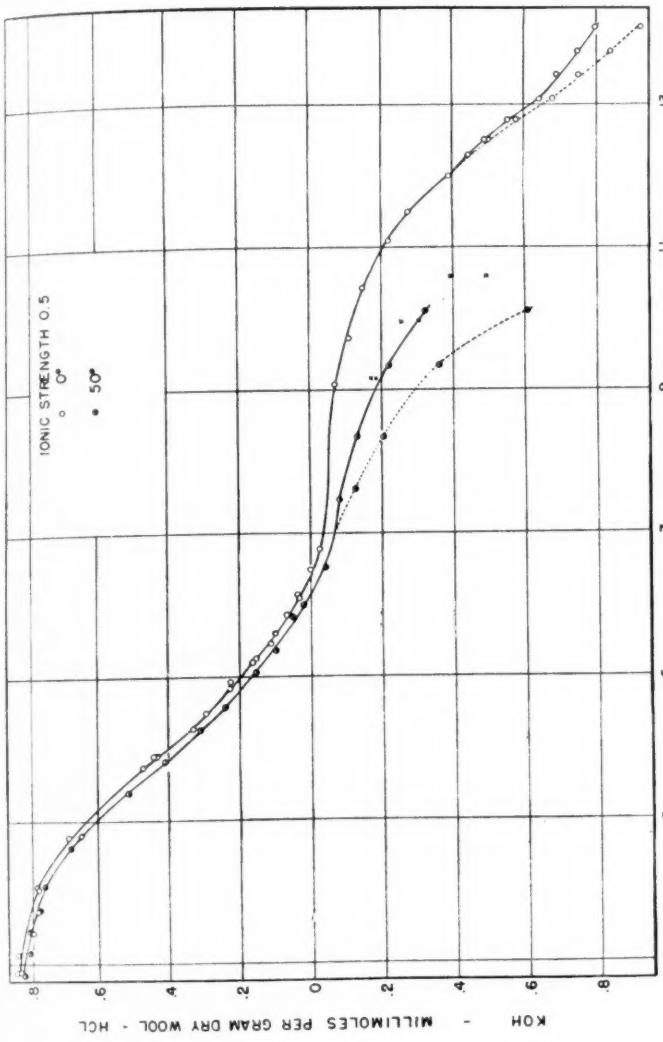

FIGURE 3.—*Combination of wool with hydrochloric acid and with potassium hydroxide as a function of* pH *and temperature, at 0.5 M ionic strength.*

combined when no account is taken of the base bound by acid groups formed in the fiber as the result of hydrolysis of disulfide bonds; the upper cross represents the same measurement properly corrected. The crosses representing the corrected measurements all fall very slightly above the solid curves, which indicates that the time allowed was somewhat short of that required for the attainment of equilibrium. Since less decomposition occurs in the shorter time interval, the uncorrected measurements lie considerably higher than the corresponding broken curves, and relatively much closer to the corrected data. It is clear that the corrections applied to the data obtained in alkaline solutions yield a much closer approximation to measurement of an acid-base equilibrium which is independent of time than do the uncorrected data, and that it is the corrected rather than the uncorrected data which should be used in the comparison of the results obtained at different temperatures.

TABLE 1.—*Combination of wool with hydrochloric acid and with potassium hydroxide as a function of temperature*

0° C.		25° C.		40° C.		50° C.	
pH	Acid or base combined	pH	Acid or base combined	pH	Acid or base combined	pH	Acid or base combined
(a) NO ADDED SALT							
	Millimoles/g		*Millimoles/g*		*Millimoles/g*		*Millimoles/g*
0.447	0.868	0.638	0.877	0.832	0.792	0.800	0.819
.635	.838	.826	.802	1.504	.685	1.103	.769
.813	.836	1.448	.687	1.790	.582	1.438	.700
.822	.812	1.710	.599	1.917	.529	1.608	.652
1.062	.779	1.915	.520	2.263	.379	1.916	.533
1.125	.789	2.191	.402	2.415	.310	2.189	.412
1.327	.748	2.406	.316	2.700	.225	2.503	.286
1.470	.735	2.722	.225	3.017	.145	2.770	.205
1.553	.708	3.093	.143	3.270	.096	3.149	.120
1.711	.652	3.370	.087	3.821	.044	3.545	.071
1.797	.629	3.962	.036	4.521	.030	3.843	.040
1.931	.574	4.603	.014	4.894	.003	4.452	.006
2.085	.522	5.257	−.013	5.629	−.006	6.37	−.013
2.228	.445	6.38	−.026	6.105	−.014	6.88	−.020
2.320	.394	6.82	−.035	6.418	−.020	6.89	−.017
2.451	.348	7.28	−.042			7.05	−.033
2.748	.247	9.56	−.070			7.24	−.035
3.039	.166	10.46	−.102			8.34	−.069
3.072	.160	10.95	−.115 (−.123)[a]			10.91	−.204 (−.312)[a]
3.272	.114	11.14	−.141 (−.153)			11.14	−.282 (−.481)
3.348	.101	11.52	−.171 (−.185)			11.40	−.341 (−.686)
3.620	.067	11.76	−.198 (−.221)			11.64	−.449 (−.958)
3.783	.060	11.96	−.252 (−.276)				
3.844	.045	12.16	−.344 (−.383)				
4.169	.022	12.40	−.440 (−.548)				
4.198	.027	12.52	−.491 (−.650)				
4.414	.017	12.71	−.561 (−.790)				
4.688	.001	12.87	−.587 (−.867)				
4.740	.012	13.16	−.716 (−1.111)				
5.140	.004						
5.58	−.012						
5.79	−.018						
6.10	−.023						
9.45	−.055						
10.01	−.067						
10.43	−.077						
10.91	−.094						
11.32	−.105						
11.37	−.097						

Footnote at end of table.

TABLE 1.—*Combination of wool with hydrochloric acid and with potassium hydroxide as a function of temperature*—Continued

0° C.		25° C.		40° C.		50° C.	
pH	Acid or base combined	pH	Acid or base combined	pH	Acid or base combined	pH	Acid or base combined
			(a) NO ADDED SALT—Continued				
	Millimoles/g		*Millimoles/g*		*Millimoles/g*		*Millimoles/g*
11.93	−.128						
12.17	−.153						
12.46	−.185 (−.187)[a]						
12.72	−.232 (−.236)						
12.88	−.297 (−.301)						
13.12	−.375 (−.379)						
13.32	−.436 (−.450)						
13.35	−.476 (−.488)						
13.49	−.565 (−.586)						
13.63	−.590 (−.610)						
13.90	−.669 (−.719)						
14.12	−.757 (−.838)						
14.24	−.702 (−.788)						
14.29	−.820 (−1.023)						
14.30	−.787 (−1.019)						
			(b) IONIC STRENGTH 0.2				
0.814	0.829	0.837	0.836			0.822	0.809
1.130	.800	1.100	.830			1.128	.792
1.433	.773	1.310	.815			1.436	.780
1.751	.753	1.725	.755			1.724	.746
1.982	.730	2.042	.729			1.953	.724
2.061	.702	2.392	.639			2.297	.677
2.378	.670	2.762	.565			2.638	.601
2.744	.595	3.333	.448			3.096	.499
2.767	.607	3.782	.334			3.615	.378
3.273	.487	4.210	.244			4.112	.279
3.571	.435	4.747	.181			4.635	.184
3.825	.372	5.107	.123			5.206	.103
4.235	.269	5.477	.085			5.511	.063
4.318	.285	5.742	.053			5.766	.032
4.359	.279	5.94	.032			6.01	.017
4.855	.177	6.23	.004			6.30	−.006
5.400	.112	6.58	−.028			6.46	−.015
5.564	.067	7.55	−.034			7.10	−.093
5.618	.083	8.34	−.077 (−.085)[a]			7.82	------- (−.146)[a]
5.94	.045	9.36	−.115 (−.125)			8.75	------- (−.197)
5.94	.030	9.98	−.162 (−.175)			9.41	−.193 (−.321)
6.29	.015	10.71	−.232 (−.264)			10.00	−.259 (−.475)
6.3	.002	11.10	−.307 (−.352)			10.22	−.294 (−.542)
6.7	−.007	11.31	−.352 (−.399)				
6.7	−.027	11.72	−.457 (−.545)				
6.75	−.010	12.11	−.541 (−.714)				
6.84	−.024	12.28	−.547 (−.743)				
7.00	−.041	12.45	−.585 (−.819)				
7.05	−.050	12.83	−.624 (−.944)				
7.68	−.050	13.16	−.720 (−1.102)				
8.28	−.093						
9.84	−.130						
10.83	−.180						
11.63	−.273						
12.23	−.391 (−.391)[a]						
12.25	−.389 (−.389)						
12.62	−.464 (−.471)						
12.68	−.495 (−.506)						
13.01	−.582 (−.602)						
13.19	−.635 (−.660)						
13.39	−.649 (−.678)						
13.41	−.640 (−.670)						
13.73	−.720 (−.760)						
13.85	−.710 (−.770)						
14.11	−.764 (−.840)						

Footnote at end of table.

TABLE 1.—*Combination of wool with hydrochloric acid and with potassium hydroxide as a function of temperature*—Continued

0° C.		25° C.		40° C.		50° C.	
pH	Acid or base combined	pH	Acid or base combined	pH	Acid or base combined	pH	Acid or base combined
(c) IONIC STRENGTH 0.5							
	Millimoles/g		*Millimoles/g*		*Millimoles/g*		*Millimoles/g*
0.477	0.868					0.436	0.947
.828	.854					.830	.828
.832	.838					1.156	.807
1.130	.850					1.458	.808
1.438	.799					1.760	.774
1.461	.810					2.090	.760
1.745	.784					2.628	.680
2.048	.781					3.388	.513
2.071	.786					3.825	.408
2.781	.687					4.266	.310
2.808	.652					4.575	.240
3.750	.471					5.069	.154
3.905	.442					5.417	.099
3.910	.432					5.843	.051
4.304	.339					6.003	.020
4.503	.294					6.53	−.042
4.887	.228					7.47	−.079
4.933	.227					7.67	−.125
5.211	.164					8.35	−.131 (−.202)[a]
5.26	.155					9.34	−.218 (−.360)
5.472	.112					10.11	−.320 (−.605)
5.61	.101						
5.870	.068						
6.10	.034						
6.14	.039						
6.5	.002						
6.78	−.024						
9.08	−.068						
9.73	−.108						
10.43	−.048						
11.09	−.220						
11.50	−.275						
12.01	−.388						
12.30	−.443 (−.443)[a]						
12.52	−.488 (−.498)						
12.80	−.552 (−.576)						
13.09	−.642 (−.678)						
13.42	−.691 (−.752)						
13.76	−.752 (−.844)						
14.09	−.792 (−.927)						

[a] Uncorrected for the effect of disulfide bond decomposition, as explained in the text.

It is apparent that the rate of decomposition increases sharply as the temperature is raised. Thus it can be seen in figure 1, representing measurements made after 24 hours, that only negligible amounts of decomposition occur at 0° C at pH values up to 13.5. At 25° C practically all the disulfide bonds are hydrolyzed at this pH within the same interval of time. At this temperature, considerable decomposition within 24 hours cannot be detected at pH values below 12.1, at which pH value decomposition is again practically complete at 50° C within the same period of time. Comparable large differences between the rates of decomposition at each of the same temperatures can be seen in figures 2 and 3.

The principal qualitative features of the comparison of the data obtained at different temperatures are common to all three sets. They are most readily distinguished in figure 1 in which the steepness of the titration curves obtained in the absence of salt results in a sharp distinction between the positions on the pH axis of the curves obtained at each temperature. It is apparent on inspection that the curves represented are relatively well separated with respect to position on

the pH axis at the alkaline end of the scale (reference is here had to the solid curves), but that their positions differ only very slightly in neutral and acid regions of pH. Indeed, the separation between the curves of acid-combination is so small in the temperature interval, 25° to 50° C, that only a single curve has been drawn through the points representing measurements made at 25°, 40°, and 50° C. Between 0° and 25° C, however, an appreciable difference in the position of the curves is found; it is in the same direction as the shift recorded in the alkaline range of pH, but it is a good deal smaller. In the intermediate range of pH values the differences in the positions of the titration curves are more difficult to evaluate, because of the very large change in pH which is required to produce a small increment in acid or base bound, and because pH measurements are least accurate in the extremely unbuffered solutions in this region of pH. The best estimates which can be made from the figure indicate a shift in the abscissas of the points in the same direction as in the other parts of the curves, as the temperature is increased. This shift is intermediate in magnitude between the small effect in the acid region and the much larger effect in the most alkaline range. Its exact magnitude is so uncertain, however, that no effort is made to evaluate it in the sections that follow.

The flatness of the titration curve determined in the absence of salt also renders the precise pH value at which neither hydrochloric acid nor potassium hydroxide is bound rather uncertain. In an earlier paper the opinion was ventured that this value was probably very nearly the same in the absence of salt as in its presence, approximately 6.4. More numerous determinations in this region now make it appear that *in the absence of salt* the pH at zero combination is in the range 4.7 to 5.1, where it has been placed by Speakman and others.

The well-marked differences in the relative magnitudes of the effects of temperature on the three main parts of the titration curves appear to be as characteristic of proteins as of their constituent amino-acids, as the recalculation of the data of Hoffman and Gortner on casein by Pertzoff and Carpenter [18, 24] and the work of Wyman on horse hemoglobin [36] have shown. They are entirely consistent with the assumption previously made that the carboxyl and amino groups of the uncombined protein are completely ionized. The effect of temperature on the acid branch of the titration curve is small because the heats of dissociation of carboxyl groups are, in general, very small. The values for different carboxylic acids are distributed about zero, so that the sign of the heat may be either positive or negative, depending on the identity of the carboxylic acid in question, and on the temperature. The changes in heat content accompanying the dissociation of hydrogen ions from the conjugate acids of imidazole and substituted ammonium bases are, on the contrary, very considerable: some 6,000 calories in the case of imidazole groups, and from 9,000 to 14,000 calories in the case of amino groups [5]. The values of the heats of dissociation of certain of the groups in wool may be estimated from the differences in the abscissas of the curves represented in the figure. In the discussion that follows this is done for the two main regions of the titration curve on either side of neutrality. No effort is made to treat separately the effect of temperature in the neutral region for the reasons already given and because the amount of imidazole groups (from histidine) in wool is, known to be very small [31].

1. DATA OBTAINED IN THE ABSENCE OF SALT

(a) COMBINATION WITH ACID

The existence of an appreciable difference between the positions of the acid combination curves at 0° and 25° C, combined with the absence of any clearly distinguishable differences between the curves at 25°, 40°, and 50° C, probably is an indication that the dissociation constants of the carboxyl groups of the protein attain a maximum value in the temperature interval 25° to 50° C, and thus probably diminish at higher temperatures. The existence of a maximum value of the dissociation constant in the temperature range of this investigation is a common characteristic of carboxylic acids [12, 14]. For these acids the curve relating the dissociation constant to temperature has a very flat maximum but becomes steeper (the dissociation constant acquires an increasing dependence on temperature) at temperatures farther from the temperature of the maximum [12]. The temperature of the maximum is about 25° C for formic acid and acetic acid but diminishes as the hydrocarbon chain attached to the carboxyl group lengthens; it is not far from 10° C in the case of *n*-butyric acid [14]. A more cogent comparison is with the constants characterizing the dissociations of the carboxyl groups of the amino-acids. No maxima have been found with glycine and alanine, which have been investigated at temperatures up to 40° and 45° C, respectively, but Harned and Embree have shown that with these amino-acids the variation of the dissociation constant with temperature at temperatures down to 10° C closely parallels the variation of the constants characterizing the simple aliphatic acids at lower temperatures, and indicates a maximum value of their dissociation constants at temperatures just above 40°. This is very close to the temperature of the maximum suggested by the present data.

Since the degree of dependence of the dissociation constants of carboxylic acids on temperature itself depends on temperature, little is gained by comparing the heats of dissociation of these groups in wool within any one temperature interval with similar quantities for related substances, such as the amino-acids. In the interval of temperature 0° to 25° C the average heat of dissociation of the carboxyl group of glycine is practically zero, of alanine is −450 calories, of glycylglycine and of glycylalanine is −600; in aspartic acid, ΔH_0^{25} (the average heat of dissociation between 0° and 25° C) or the carboxyl group next to the amino group is +1,600; for the same group in glutamic acid it is +1,900. The values of ΔH_0^{25} of the γ and δ carboxyl groups, of these amino-acids are +2,100 and +1,040 calories, respectively [5]. Since the latter are the carboxyl groups which are presumably free in proteins to react with base, the acid branch of protein titration curves should be determined by the number of these groups and their properties.

Certain complications enter into the calculation of ΔH from titration data in the case of proteins because they are polybasic. ΔH may be calculated from the shift in the abscissas of the titration curves of a monobasic acid or base, or of a polybasic acid with dissociating groups which have widely different strengths, because for such acids the difference in pH at which a given amount of base or acid is bound at two different temperatures represents the logarithm of the ratio of

the dissociation constants of a single acidic or basic group ($\Delta pH = -\log K_2/K_1 = -\Delta \log K$).[9] From this change in K produced by a change in temperature it is possible to calculate the average value of ΔH in the same interval of temperature by means of the integrated form of the Van't Hoff equation:

$$\Delta H_{T_1}^{T_2} = 4.5787 \frac{T_2 T_1}{T_2 - T_1} \Delta \log K. \quad (1)$$

The values cited above have been so calculated. It has been shown by Simms [25], Weber [33], von Muralt [32], and others that the titration curves of polybasic acids which contain identical dissociating groups far enough apart from one another in the molecule to have no influence on the dissociation of one another may be described by an expression which is functionally identical with the law of mass action for a monobasic acid. For such hypothetical acids, ΔH per mole of dissociating groups may be calculated exactly as in the simpler cases described above, by means of the relationship $\Delta pH = -\Delta \log K$. This can be done even in certain other cases when no restriction is placed on the interrelationships of the values of all the K's, as Wyman has shown in a general and mathematically rigorous analysis of the effect of temperature on the titration curves of polybasic acids. Wyman came to the conclusion that in any region of pH in which ΔpH is practically independent of pH, ΔpH can be equated to $-\Delta \log K$ for some one dissociating group or set of groups with a good degree of approximation.[10] Calculation of ΔH from ΔpH in regions of transition from one constant value of ΔpH to another does not correspond to any one set of similar dissociation equilibria, and gives values intermediate to those characterizing the homogeneous sets of dissociating groups in the pH regions on either side of the region of the transition.[11]

Thus by making the reasonable assumption that the titration curves of proteins are determined by the relative acid strengths of distinct, essentially nonoverlapping sets of similar dissociating groups, one may obtain values of $\Delta \log K$ in each of the two main regions of pH values of the present data for wool and compare them with similar results obtained by Pertzoff and Carpenter with casein, and by Wyman with hemoglobin. The results of this comparison, and a comparison of the corresponding values of ΔH, are given in table 2.

[9] The use of pH differences and of ratios of constants avoids practically all of the theoretical difficulties that arise in attempting to evaluate the constants themselves from titration data alone. Thus ΔH can be calculated more simply and more certainly than any single value of K. The only factor left out of account in this method of calculation is the change of activity coefficients with temperatures of ions other than the hydrogen ions, but the temperature dependence of such activity coefficients is known to be very small.

[10] Unless groups possessing distinct values of ΔH chance to possess the same dissociation constants. In this case, the average heat of dissociation for all the groups would be given.

[11] Kern [19, 20], Cannan [3], two of the present authors [29], and others, have shown that the interaction between many like dissociating groups in highly polybasic acids, such as proteins, often introduces an empirical fractional exponent (equal, or nearly equal to 0.5 and practically independent of temperature) to the hydrogen-ion activity term in the simple law of mass-action equation which would characterize their behavior in the hypothetical simple case. At first sight, this might appear to indicate that the term $\Delta \log K$, used in calculating ΔH by means of eq 1, is not equivalent to $-\Delta pH$ (the difference in the pH coordinates of the titration curves obtained at T_2 and T_1) but is equal to ΔpH multiplied by the same empirical exponent. Two considerations, however, show that this does not follow as a rigorous consequence of the use of the exponent: (1) The constant in the modified equation is not to be identified with the true dissociation constant of any one group or set of groups; it is a function of all the constants of all the groups, and these are widely distributed in magnitude as a result of mutual interaction. (2) It is a matter of observation that the numerical value of the empirical constant corresponds very well to the square root of the unmodified mass-law constant that might be expected to characterize the dissociation of the groups if no interaction occurred (in proteins the midpoint of the carboxyl curve comes at pH 4.2, close to the pK of carboxyl groups in polypeptides, while $-\log K$ in the empirical equation containing the exponent is 2.1). Thus the equation might well be written $K = k_{\text{monobasic}}^{0.5} = \frac{[H^+]^{0.5}[A^-]}{[HA]}$. From this it would follow that $\Delta \log K_{\text{monobasic}} = -\Delta pH$ and not $-0.5\,\Delta pH$.

TABLE 2.—*Calculation of average heats of dissociation of carboxyl groups in wool and other proteins, in the absence of salt*

Protein	pH range studied	Temperature range	$-\Delta pH$	ΔH, if $-\Delta pH = \Delta \log K$
		°C		cal/mole
Wool	1 to 5	0 to 25	0.16	+2,380
		25 to 50	±.03	±500
Horse hemoglobin	4.3 to 6	6.5 to 25	----------	−2,000 to −3,000
		25 to 37.5	----------	
Casein [1]	2 to 5	22 to 35	±.1	±3,000

[1] The data on casein are subject to considerably larger uncertainties than the data for the other 2 proteins.

It is apparent that the heat of dissociation of the acid groups of wool in the lower temperature interval is very close to the values that characterize carboxyl groups in dibasic amino-acids, albeit slightly higher. In the higher temperature interval the heat of dissociation is very much smaller, as it must be in the region of a maximum value of K, where ΔH approaches zero. The values found with casein agree with those for wool as closely as should be expected, considering the low intrinsic accuracy of the casein data and the fact that different ranges of temperature were used. The data of Wyman for horse hemoglobin do not extend below pH 4.3, and thus cover only a small fraction of the range of the present comparison. Over this range the sign of ΔpH is opposite to that of the values of ΔpH characterizing the data for wool and indicates a *negative* heat of 2,000 to 3,000 calories. This difference in sign is not as important for the purpose of the present comparison as is the small magnitude of ΔH. This qualitative agreement acquires further significance when the comparison is extended to other regions of pH where the heats of dissociation of all three proteins are much larger. A possible explanation of the difference in sign between the results with wool and with hemoglobin is suggested later in this paper.

The fact that the dissociation constants of the carboxyl groups of wool have a maximum value at a temperature near 40° has an important consequence in relating the titration data reported in this paper to the acidic properties of wool at the high temperatures, near the boiling point of water, to which wool is exposed in dyeing. At these high temperatures the position of the acid titration curve on the pH coordinates is probably near its position at 0°, the temperature at which the influence of various factors has been studied in greatest detail [29].

(b) COMBINATION WITH BASE

On the alkaline side of neutrality, the titration curves of wool at the different temperatures are widely separated and show every indication of being nearly, if not exactly,[12] parallel at pH values above 10. Two nearly equal intervals with respect to the pH axis separate the curves for the three different temperatures.

In calculating values of ΔH for the acid branch of the titration curve, it was possible to proceed on the approximately valid assumption that only carboxyl groups, from aspartic and glutamic acids, determined the course of this part of the curve. On the alkaline side of the curve dissociation equilibria of two widely dissimilar basic groups, the ϵ-amino groups of lysine and the guanidino groups of

[12] The curves were drawn freehand without attempting to make them parallel.

arginine, as well as the dissociation of one acid group, the phenolic radical of tyrosine, may all be involved within a narrow range of pH. The relation of ΔpH to Δ log K for any one of these sets might therefore be fairly complex. Because the curves appear to be nearly parallel over a wide range, however, one may follow the procedure justified by Wyman, substituting values of $-\Delta$pH in place of Δ log K in eq 1, for each interval of temperature. The results of this treatment of the data are represented in table 3, in which it is apparent that a fairly uniform separation (probably within experimental error), and therefore a fairly constant value of ΔH, is found for the entire alkali combination curve. The values in which the greatest discrepancies appear are obtained in the region of pH in which very small amounts of base are combined. Here the curves are so nearly flat that a very small error in the measurements, or in the corrections for ash, results in large discrepancies in the pH coordinates at which these quantities of base are bound. For this reason, and because the number of imidazole groups in wool is so small as to account for only a very small amount of acid or base bound, no effort is made to evaluate ΔH in the intermediate range of pH values near neutrality.

TABLE 3.—*Calculation of average heats of dissociation of groups in wool dissociating at* pH *values above 6*

0° to 25° C			25° to 50° C		
Base bound per gram	−ΔpH	ΔH_0^{25}	Base bound per gram	−ΔpH	ΔH_{50}^{25}
Millimoles			*Millimoles*		
0.1	0.75	11,190	0.1	1.47	25,820
.2	.81	12,070	.2	1.04	18,310
.3	.85	12,640	.3	0.84	14,800
.4	.88	13,100	.4	.78	13,720
.5	.89	13,240	.5	.84	14,800
.6	.83	12,380	----------	---------	----------
.7	.81	12,030	----------	---------	----------
Average	----------	12,380	----------	---------	----------

The numerical values of ΔH tabulated are very close to those, ranging from 10,000 to 13,000 calories per mole [5], which would be expected to characterize the dissociation of hydrogen ions from the conjugate acid forms of amino or guanidino groups in amino-acids. They are about twice as great as the values to be expected if the acid dissociation of the hydroxyl group of tyrosine were being measured in any part of this region [9, 34], and appear to support the suggestion made earlier [29] that the hydroxyl groups of tyrosine may not be titrated by base in the region of pH covered by this investigation. The values, although consistently slightly higher, are in fair agreement with the figure, 11,500 calories, found by Wyman for horse hemoglobin, and with an approximate value of 14,000 calories which may be deduced from the figures given by Pertzoff and Carpenter, for casein.

The fact that the values for wool and for casein are so nearly equal to the heat of dissociation of water (13,481 calories at 25° [13]) shows that the effect of temperature on the amounts of base bound at any constant *hydroxyl-ion* activities (as for example in a given solution of sodium hydroxide) would be very small. Thus it is only because

the amounts of base bound are compared on a scale of *hydrogen-ion* activities that the very considerable temperature effect appears. It is the latter basis of comparison which has significance in terms of *acidic* dissociation constants, used consistently throughout this paper.

The degree of agreement with the results for other proteins may be construed as furnishing additional support for the validity of the corrections for alkaline hydrolysis of disulfide bonds included in the calculations of the amounts of base bound. Thus if ΔH were calculated from the difference in the pH coordinates of the broken curves, representing the uncorrected measurements, very high values of ΔH (20,000 to 25,000 calories), entirely without precedent in investigations of amino acids and proteins, would result. These values would not be independent of time, but would increase with increasing periods of exposure of the wool to alkali. Thus only the values calculated from the corrected measurements and tabulated in table 2 may be interpreted thermodynamically.

Regardless of what detailed significance may be attached to the values shown in table 2, they are, in combination with the much smaller values characterizing the acid branch of the curve, entirely consistent with the view that the process of titration with acid consists in the replacement of hydrogen ions on the ionized carboxyl groups of the uncombined protein while the process of titration with alkali consists predominantly in the removal of hydrogen ions from the conjugate acids of the amino and guanidino groups.

2. DATA OBTAINED AT CONSTANT IONIC STRENGTH

The data obtained in the presence of constant concentrations of chloride or potassium ions show a different functional relationship between the amounts of acid or base bound and pH [29]. However, the effect of temperature upon this relationship is so similar to its effect on the data obtained in the absence of salt that one may without further discussion tabulate representative values of ΔpH taken from figures 2 and 3 and also the values of ΔH calculated from them. This has been done in table 4.

It will be seen at once that the average of the values of ΔH calculated for the acid region of the curve for 0.2 *M* ionic strength in the temperature interval 0° to 25° C (table 4) is very close to the value 2,380 given in table 2 for this quantity in the absence of salt. The individual values fluctuate considerably, but this is largely a consequence of the manner in which the freehand curve through the data has been drawn. In the higher temperature interval, 25° to 50° C, there is practically no effect of temperature, just as in case of the data obtained with acid alone. The resemblance between these sets of data extends into the alkaline region, although here again there is great fluctuation among the individual values. It is possible that the drift from 11,000 to 12,000 calories, characterizing the middle portion of the alkaline curves, to 7,000 to 8,000 calories at their most alkaline end is a real phenomenon and represents transition at 0.5 to 0.6 millimole of base bound from the titration of amino groups to the titration of tyrosine hydroxyl groups when more base is combined.[13]

[13] Recent work in this laboratory on the combination of base by silk, in which most of the acidic groups are phenolic, indicates that the hydroxyl groups of tyrosine dissociate hydrogen ions in this region of pH values.

However, this supposition is not easily reconciled with the failure of a differential effect to appear in the measurements made in the absence of salt nor with the expected relative strengths of tyrosine hydroxyl and arginine guanidino groups. An extreme fluctuation, resulting in a change of sign of ΔH, is found in the region of very small amounts of combined base. As in the data obtained without salt, this may be ascribed to the small slope of the titration curve in this region, and the resulting large effect of ΔpH which slight changes in the drawn curves, or slight errors in corrections for ash, would produce. Wide fluctuations are also found in the data listed for the interval 25° to 50° C, but the average of the values given is 15,060 calories, in good agreement with most of the individual values in table 3 for this temperature interval.

TABLE 4.—*Average heats of dissociation of acidic and basic groups in wool calculated from titration data obtained at constant ionic strength*

IONIC STRENGTH 0.2

ACID REGION			ALKALINE REGION		
0° C to 25° C			0° C to 25° C		
Acid bound	−ΔpH	ΔH_0^{25}	Base bound	−ΔpH	ΔH_0^{25}
Millimoles/g		*Calories*	*Millimoles/g*		*Calories*
0.1	0.17	2,540	0	0	0
.2	.17	2,540	.1	−.13	−1,940
.3	.28	4,170	.2	+.64	+9,540
.4	.26	3,880	.3	.75	11,180
.5	.17	2,540	.4	.82	12,200
.6	.11	1,640	.5	.82	12,200
.7	.06	890	.6	.58	8,650
			.7	.50	7,450
Average		2,600			
25° C to 50° C			25° C to 50° C		
Acid bound	−ΔpH	ΔH_{25}^{50}	Base bound	−ΔpH	ΔH_{25}^{50}
Millimoles/g		*Calories*	*Millimoles/g*		*Calories*
0.1	0.03	530	0	0.34	5,990
.2	0	0	.1	1.31	23,100
.3	0	0	.2	0.95	16,710
.4	0	0	.3	.82	14,430
.5	0	0			
.6	0	0			
.7	0	0			

IONIC STRENGTH 0.5

0° C to 50° C			0° C to 50° C		
Acid bound	−ΔpH	ΔH_0^{50}	Base bound	−ΔpH	ΔH_0^{50}
Millimoles/g		*Calories*	*Millimoles/g*		*Calories*
0.1	0.17	1,370	0	0.325	2,620
.2	.17	1,370	.1	1.84	14,820
.3	.15	1,210	.2	1.77	14,240
.4	.16	1,290	.3	1.67	13,470
.5	.15	1,210	.325	1.61	12,900
.6	.15	1,210			
.7	.16	1,290			
Average		1,280			

The data obtained at an ionic strength of 0.5 exhibit smaller fluctuations and are numerically in good agreement with the values for ΔH obtained in the other sets of experiments. The average value of ΔH_0^{50} in the acid region is only 1,280 calories, but it has already been shown that practically all of the effect of temperature in the acid region is manifested in the lower half of this large interval of temperature. It is justifiable, therefore, to use double this figure, or 2,560 calories, as the value of ΔH_0^{25} for comparison with the other sets of data. In the alkaline region the individual values of base bound between 0.1 millimole/g and 0.325 millimole/g are constant within the error of the measurements and are close to those found in the other sets of data. Owing to the large amounts of decomposition at this temperature, the measurements do not extend sufficiently far into the alkaline region to determine whether the apparent fall in the values of ΔH found at 0.2 ionic strength would be found in these experiments also.

3. COMPARISON WITH CALORIMETRIC DATA

It is of interest to compare the present estimates of 2,380, 2,600, and 2,560 calories for the heat of dissociation of the carboxyl groups of wool in the temperature interval 0° to 25° C with the experimental value for the heat evolved at 0° per equivalent of hydrochloric acid combined by wool, as determined directly by a calorimetric method by Speakman and Stott [27]. The value obtained by these authors was 3,560 calories, significantly higher than our own figure. In calculating this quantity, Speakman and Stott assumed that there were only negligible differences between the titration curves of wool at 22.2° and 0°; this was done in order to estimate the amount of acid combined at each pH from a titration curve obtained at 22.2°. The error introduced by this approximation may easily approach 1,000 calories in the calculated result when less than half the maximum amount of acid is bound. However, this source of error should be practically negligible when high concentrations of acid are used, since then the amount of acid combined is independent of small changes in pH and temperature. Under these conditions, the heat of dilution of the acid is also relatively large, and the heat of reaction, calculated as the difference between the heat of dilution and the total heat evolved, is subject to a larger uncertainty. Nevertheless, the values obtained with high concentrations of acid are probably not subject to an error of more than two or three hundred calories. They appear entirely consistent with the value reported here; the higher value of Speakman and Stott refers to 0°, while the value obtained by the titrimetric method of the present paper is the average of a very low value at 25° and an appreciably higher value at 0°.

It should be pointed out that the measurements made by Speakman and Stott were not interpreted by these authors as heats of dissociation of the carboxyl groups, but rather as the heats of reaction of the *basic* (amino) groups with acid. Since the value obtained was very much lower than the value which usually characterizes the neutralization of a base by an acid, Speakman and Stott concluded that the value was so low as to indicate that the basic side chains of wool were not free but were combined with acid side chains to form salt linkages, as these authors had previously suggested. However, since wool is an ampholyte and in the uncombined form a dipolar ion as well, it is

clear that the heat measured was not analogous to the heat of neutralization of a base by an acid, but to the heat of association of hydrogen ions with carboxylate ions. Hence the results obtained provide no evidence either for or against the existence of salt linkages.[14] It is evident that calorimetric measurements of the heat of combination of wool with *base*, had they been made, would have led Speakman and Stott, by the same process of reasoning, to a different set of conclusions.

4. SIGNIFICANCE OF THE HEATS OF DISSOCIATION

The estimated values of ΔH reported in this paper have been calculated by assuming that when the pH values at which a fixed amount of base is bound at two different temperatures are compared, under certain conditions $\Delta\text{pH} = -\Delta \log K$. The justification for relating ΔpH to a change in the logarithm of a hydrogen-ion dissociation constant, characterizing a single set of dissociating (acid) groups in the conventional formulation of the dissociation equilibria for a dissolved protein, has already been cited and discussed. It remains to enquire whether this method of analysis is equally valid for the theory of the titration curve of wool presented in an earlier paper [29], which assumed that anions of the acids used, as well as hydrogen ions, are only partially dissociated from the protein.[15] In terms of this theory, the positions of the curves of acid combination, with respect to the pH axis, are determined not by log K, where K is a conventional hydrogen-ion dissociation constant, but, to a high degree of approximation, by log $K_H'K_A'$, where K_H' is the hydrogen-ion dissociation constant characterizing the equilibrium,

$$WHCl \rightleftarrows WCl^- + H^+, \tag{2}$$

and K_A' is the constant characterizing the dissociation equilibrium,

$$WCl^- \rightleftarrows W^* + Cl^-, \tag{3}$$

in which W^* represents wool in the uncombined state, and the other symbols have their familiar chemical significance. The position of curves obtained in the absence of salt is determined approximately by 1/2 log $K_H'K_A'$ rather than by log $K_H'K_A'$ [29].

It is apparent therefore that in the presence of a constant anion concentration, ΔpH represents the sum of $\Delta \log K_H'$ plus $\Delta \log K_A'$. In the absence of salt it is approximately equivalent to one half of this quantity. Thus, the heat of dissociation calculated by inserting $-\Delta$pH in place of $+\Delta \log$ K in the Van't Hoff equation is actually the sum of two heats of dissociation, associated with reactions (2) and (3).

It is of interest, therefore, to determine what part of the total heat effect is to be attributed to each of the two constituent equilibria. An estimate of the distribution in the case of combination with acid may be made as follows: It has been shown that at high concentrations of

[14] The values obtained by Speakman and Stott with monochloracetic acid are essentially the same as with hydrochloric acid over the part of the titration curve in which the amounts of monochloroacetic acid combined at a given pH are the same as the amounts of hydrochloric acid combined. Much lower values of ΔH are obtained at high concentrations of the partially dissociated acid when large excess amounts of acid are bound. This indicates that the heat of combination of wool with the *excess* acid is very low or zero. Direct measurements of the heat of combination of this excess acid now in progress in this laboratory show that this is indeed the case.

[15] This theory, originally proposed to explain the large scale effects of the concentration of added neutral salts on the position of acid-combination curves for wool on the pH axis, has since received additional support [30].

chloride the position of the titration curve with respect to the pH axis is practically independent of K_A'. The effect of temperature on the midpoint pH of curves obtained under these conditions must therefore be attributed in its entirety to an effect upon K_B'. This effect has been estimated (table 4) as some 2,500 calories. Since the effect of temperature upon K_B' must be invariant, regardless of whether or not salt is present, a contribution to ΔpH in the absence of salt of approximately one-half the amount found at high concentrations must be ascribed to the temperature effect on this constant. This contribution to ΔpH, about 0.08 unit, also happens to be just half of the total effect of temperature (expressed as ΔpH) found when salt is absent. Since the remaining half of the pH shift produced by a change in temperature under these conditions must be ascribed to the effect of temperature upon K_A', it is clear that the heats of dissociation of hydrogen ions and of chloride ions are approximately equal, and that the sum of the heat changes associated with the two sets of equilibria (2) and (3) is roughly double the values calculated from ΔpH under either set of conditions.

In drawing conclusions from a comparison of the numerical results obtained in this investigation, or by the calorimetric method of Speakman and Stott, with those reported for amino-acids and proteins in *solution*, a certain caution is desirable. The reaction of dissolved acid with a dissolved ampholyte involves only changes in heat content which may be described as heats of reaction and heats of mixing (the latter is small). The reaction of dissolved acid with wool involves in addition a heat change equivalent to a heat of adsorption or a heat of condensation in that quantities of acid are transferred from a large volume, that of the aqueous phase, to a small volume, that of the fiber.

Thus the total reaction may be separated into two steps:

$$(H^+)_{aq} \rightleftharpoons (H^+)_{wool} \tag{4}$$

$$(H^+)_{wool} + WCOO^- \rightleftharpoons WCOOH, \tag{5}$$

in which the first equation represents the transfer of ions to the wool phase, and the second represents the reaction of the ions with the groups in wool which combine with them. The heat effect estimated by substituting ΔpH for Δ log K in the Van't Hoff equation represents the sum of the heat changes involved in the two equilibria represented in eq 4 and 5 rather than the heat of dissociation corresponding to eq 5 alone. The latter can only be obtained by estimating, if possible, the heat change corresponding to eq 4 and subtracting it from the total heat. The magnitude of the heat of the transfer represented in eq 4, which is brought about at the expense of the chemical potential energy of the reactants, may be estimated by calculating the entropy change at equilibrium from purely geometrical considerations, if it is assumed that there is no important difference between the two phases with respect to the degree of interaction within them of the ions with one another, or with the solvent. This calculation may be made with sufficient exactness for the present purpose from the approximate relation

$$\Delta S = nRT \ln \frac{V_{aq}}{V_w}, \tag{6}$$

in which n is the number of moles compressed into the volume of the wool phase, V_w, from the volume of the aqueous phase, V_{aq}, and ΔS is the entropy change. This simplified equation leaves out of account the entropy-change contribution from the dilution of the hydrochloric acid remaining in the aqueous phase at equilibrium, but when the acid is initially more dilute than 0.01 M, under the conditions of the present experiments, the final concentration is so low as to make this contribution small.[16] No distinction is made in this method of treatment between the molal entropy change between the initial and final states and the molal entropy change for an infinitesimal change at equilibrium, although it is only the latter which, multiplied by T, may be equated to ΔH in any actual system. In the present case, only the entropy changes inherent in the dimensions of the system, and therefore only those characteristic of an ideal gas, are under consideration; therefore, the two molal entropies cited will be identical.

Substituting in eq 6 numerical values from representative experiments in which low initial concentrations of acid were used, and which therefore correspond fairly closely to the standard state conditions at which ΔH is defined, the ratio V_{aq}/V_w becomes very nearly 100, and $T\Delta S(=\Delta H)$ at 0° C is approximately 2,500 calories per mole of acid transferred. This figure is close to the figure calculated from the data in the acid region. Thus the heat of dissociation of a hydrogen ion from a carboxyl group in wool in the temperature interval 0° to 25° C, *exclusive of the heat of transfer of acid between phases*, may be very much less than the value reported here, and may even be negative, as in the corresponding values obtained by Wyman with horse hemoglobin. The fact that the heats of dissociation obtained from the alkali-combination curves of wool are also somewhat higher than the corresponding values reported by Wyman is entirely consistent with this suggestion. A similar contribution to the effect of temperature on the pH coordinates of titration measurements must be expected in all heterogeneous systems, whether they are of such a nature as to be amenable to treatment by means of the Donnan membrane equilibrium equations or require the type of stoichiometric anion-association analysis applied to wool protein by the present authors.

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IV. REFERENCES

[1] E. Q. Adams, J. Am. Chem. Soc. **38,** 1503 (1916).
[2] N. Bjerrum, Z. physik. Chem. **104A,** 147 (1923).
[3] R. K. Cannan, Cold Spring Harbor Symposia in Quantitative Biology **6,** 1 (1938).
[4] R. K. Cannan and B. C. J. G. Knight, Biochem. J. **21,** 1384 (1927).
[5] E. J. Cohn, Ergeb. Physiol. **33,** 781 (1931).
[6] E. J. Cohn, in J. M. Luck, Annual Review of Biochemistry, Stanford University, **4,** 93 (1935).
[7] E. J. Cohn, Chem. Revs. **19,** 241 (1936).

[16] In addition, this part of the entropy change is also present when all the reactants are dissolved, and should not be included in the present estimate of the entropy of condensation which is peculiar to the reaction in two phases.

[8] J. A. Crowder and M. Harris, J. Research NBS **16,** 475 (1936) RP885.
[9] J. B. Dalton, P. L. Kirk, and C. L. A. Schmidt, J. Biol. Chem. **88,** 589 (1930).
[10] F. L. Goodall and C. Hobday, J. Soc. Dyers Colourists **55,** 529 (1939).
[11] J. P. Greenstein, M. Kiese, and A. B. Hastings. [Unpublished.]
[12] H. S. Harned and N. D. Embree, J. Am. Chem. Soc. **56,** 1050 (1934).
[13] H. S. Harned and W. J. Hamer, J. Am. Chem. Soc. **55,** 2194 (1933).
[14] H. S. Harned and B. B. Owen, Chem. Revs. **25,** 31 (1939).
[15] L. J. Harris and T. W. Birch, Biochem. J. **24,** 1080 (1930).
[16] M. Harris and H. A. Rutherford, J. Research NBS **22,** 535 (1939) RP1203.
[17] D. I. Hitchcock and A. C. Taylor, J. Am. Chem. Soc. **59,** 1812 (1937).
[18] W. F. Hoffman and R. A. Gortner, Colloid Symposium Monograph **2,** 209 (The Chemical Catalog Co., New York, N. Y., 1925).
[19] W. Kern, Z. physik. Chem. **189A,** 249 (1938).
[20] W. Kern, Biochem. Z. **301,** 338 (1939).
[21] B. B. Owen, J. Am. Chem. Soc. **56,** 1695 (1934).
[22] B. B. Owen, J. Am. Chem. Soc. **57,** 1526 (1935).
[23] W. I. Patterson and M. Harris. [In preparation for publication.]
[24] V. A. Pertzoff and S. C. Carpenter, J. Gen. Physiol. **16,** 257 (1932).
[25] H. S. Simms, J. Am. Chem. Soc. **48,** 1239 (1926).
[26] A. Sookne, C. H. Fugitt, and J. Steinhardt, J. Research NBS **25,** 61 (1940) RP1314; Am. Dyestuff Reporter **29,** 333 (1940); Textile Research **10,** 380 (1940).
[27] J. B. Speakman and E. Stott, Trans. Faraday Soc. **34,** 1203 (1938).
[28] J. Steinhardt. [In preparation for publication.]
[29] J. Steinhardt and M. Harris, J. Research NBS **24,** 335 (1940) RP1286; Am. Dyestuff Reporter **29,** 103, 311 (1940); Textile Research **10,** 269 (1940).
[30] J. Steinhardt and M. Harris, Proc. Am. Soc. Biol. Chemists, J. Biol. Chem. **133,** xcvii (1940).
[31] H. S. Vickery and R. J. Block, J. Biol. Chem. **86,** 107 (1930).
[32] A. L. Von Muralt, J. Am. Chem. Soc. **52,** 3578 (1930).
[33] H. H. Weber, Biochem. Z. **189,** 381 (1930).
[34] P. S. Winnek and C. L. A. Schmidt, J. Gen. Physiol. **18,** 889 (1934–35).
[35] J. Wyman, Jr., Chem. Revs. **19,** 213 (1936).
[36] J. Wyman, Jr., J. Biol. Chem. **127,** 1 (1939).

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STANDARD ELECTRODYNAMIC WATTMETER AND AC-DC TRANSFER INSTRUMENT

By John H. Park and Arthur B. Lewis

ABSTRACT

A description is given of the design and construction of the standard instrument used at the National Bureau of Standards in testing wattmeters and watthour meters.

The investigation to determine the accuracy of this instrument for alternating-current testing at frequencies up to 2,000 cycles per second is described and the results are given.

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I. INTRODUCTION

The basic units for electrical measurements are maintained at the National Bureau of Standards by the use of standard cells and standard resistors. The corrections to be applied to the indications of d-c measuring instruments can therefore be readily and accurately determined by using secondary standards, which have been directly compared with these primary standards, in conjunction with potentiometers and volt boxes. Since the primary standards are maintained by means of d-c measurements, the determination of the corrections to be applied to the indications of a-c instruments must involve at some point the use of a secondary standard or transfer instrument. This transfer instrument must be such that its reading or indication is the same with direct current as with alternating current , or differs by a known amount. The standard instrument is calibrated [1] on reversed direct current [2] and this calibration is then transferred to its a-c indications, hence the name.

Such transfer instruments are used in two separate and distinct kinds of tests: (1) in the transfer testing of a-c ammeters, voltmeters, and wattmeters which are of types that can be used on either alternating or direct current, and (2) in the straight testing with alternating current of voltmeters, ammeters, wattmeters, and watthour meters of types that are not suitable for use on direct current. In making the transfer test, the instrument under test is first tested, or calibrated, using the average of the reversed d-c values. The instrument under test and the standard transfer instrument are then so connected as to respond to the same current, voltage, or power. The current on both instruments is then adjusted until the instrument under test comes to the desired scale point and the standard instrument is read. A series of readings, using alternately direct and alternating current, is obtained, and the difference between the mean of the readings obtained with alternating current and that of those with direct current is computed from these data. This procedure very completely eliminates all sources of error—such as heating, shift of zero, and reading error of either instrument—and leaves in the net difference only those errors which arise from sources such as inductance, capacitance, and eddy currents, in which the effect on alternating current differs from that on direct current. The transfer instruments have been carefully studied and any such effects in them are small and definite and can readily be allowed for, so that the net error of the instrument under test on alternating current relative to its performance on direct current is thus determined.

In a straightforward test with alternating current the transfer instrument is calibrated by applying reversed direct current to it alone. It is then used as a standard, and the readings of the instrument under test are compared with it, using alternating current. The standard transfer instrument is calibrated on reversed direct current before and after it is compared at any scale point with the instrument under test. This procedure has to be used when the a-c instrument is of such nature

[1] "Calibrate" as used in this paper means the determination of the relation between the indications of, for example, a wattmeter and the true watts.

[2] The expression "reversed direct current" is used to designate the regular procedure in the use of instruments of this kind on direct current in order to avoid error caused by the local magnetic field. For example, in using an electrodynamic wattmeter on direct current, two readings are taken, the direction of current flow through the instrument being reversed before taking the second reading. The mean of the two readings gives a result independent of the local magnetic field.

that it does not respond to direct current, and with all instruments the range of which exceeds the range (10 amp and 300 v) of the standard transfer instruments. In this latter case instrument transformers must be used to extend the range of the transfer instrument. It may be noted that any self-heating or shift of zero which occurs in the instrument under test during the course of this straight a-c test will be included in the final result, and the accuracy of a test of this type is therefore definitely less than that of the transfer test.

The transfer instruments usually used at the National Bureau of Standards are of the electrodynamic type. The voltmeter in use at the present time has been described in a previous publication.[3] The present paper describes the wattmeter now being used. Although designed primarily as a wattmeter, this instrument may also be used as an ammeter if it is connected to measure the power consumed in an external shunt.

II. DESIGN AND CONSTRUCTION

1. CRITERIA OF DESIGN

A transfer instrument to be satisfactory for the type of testing work done at the National Bureau of Standards should possess, so far as possible, the following desirable characteristics:

(1) The frame of the instrument should be made from a nonmagnetic, nonconducting material. This material should lend itself to a sufficiently sturdy and permanent construction to avoid future difficulties resulting from warping of the instrument frame and consequent sticking of the moving system.

(2) The zero drift of the instrument on steady deflection should be as small as possible.

(3) The sensitivity of the instrument should be such that a change of 0.01 percent of the total deflection can be detected readily and with certainty on all ranges.

(4) The ac-dc differences of the instrument, that is, the differences between the indications of the instrument on alternating current and the average of its indications on reversed direct current, should be negligible for power frequencies and as low as possible for somewhat higher frequencies.

(5) The instrument should be astatic in construction.

(6) The damping of the moving system should be slightly less than critical.

(7) The response time[4] of the instrument should be reasonably short, preferably not greater than 10 sec.

(8) The two moving coils, the reflecting mirror, and the damping vane should be rigidly interconnected in order to avoid forced vibrations of these parts with respect to each other.

(9) The indication of the instrument should be read easily and with a minimum of eyestrain.

(10) The moving system should be suitable for use on voltages up to 300 v, and the fixed-coil system should have a primary current range of 5 amp and such additional ranges as can be obtained without undue difficulty.

[3] F. K. Harris, *A suppressed-zero electrodynamic voltmeter*, BS J. Research **3**, 445 (1929) RP105.

[4] The response time of an instrument is the time required for the pointer of the instrument to come to apparent rest after a change in the value of the measured quantity.

These desirable characteristics are listed in their approximate order of relative importance as determined largely by the previous experience of members of the staff in the construction and use of similar instruments. It was proposed to incorporate these characteristics in the construction of the new instrument so far as was compatible with their sometimes conflicting requirements.

2. GENERAL FEATURES OF DESIGN

Since pivot friction could seriously limit the sensitivity attainable, pivots are not used but the moving system is suspended from top and bottom on two phosphor-bronze ribbons. The deflection of the instrument is read on a ground-glass scale by means of a beam of light reflected from a small mirror attached to the moving system. The distance from mirror to scale is 2 m, giving the instrument an effective scale length, at full-scale deflection, of about 4 m. The instrument is made astatic by using two sets of moving and fixed coils, one placed slightly above the other, the direction of winding of one set of coils being reversed with respect to the direction of winding of the other. Air damping is provided by mounting a rectangular damping vane on the moving system and having it rotate within a fixed damping box. In order to obtain the most nearly linear relation between deflection and power being measured, the moving coils are held near the position of zero mutual inductance between the fixed and moving coils when the moving coils are deflected to their full-scale position. This is accomplished by resetting the series resistor in the voltage circuit for each nominal value of watts being measured. The mechanical zero of the instrument need not be disturbed, and the deflection of the moving system is thus approximately the same, regardless of the nominal value of watts being measured. The result is to minimize the zero shift, on steady deflections, resulting from the inelastic yielding of the spring and suspensions. This means, in turn, that it is permissible to make less frequent calibrations of the instrument on direct current when it is being used as a standard a-c wattmeter or ammeter.

3. DETAILS OF DESIGN AND CONSTRUCTION

(a) SUPPORTING FRAMEWORK

One of the chief difficulties encountered with previous transfer instruments has been warping of the supporting framework, which resulted in sticking of the moving system. The difficulty of locating and removing the causes of this misalinement, and the consequent sticking, led to the conclusion that the framework of the new instrument should be made of materials less subject to warping than wood and which preferably allowed some degree of vision within the instrument. Since all metallic materials are out of the question because of eddy-current or magnetic errors, the field of choice was very limited. After some discussion it was decided to use glass for the supporting framework, since it is nonwarping and nonmagnetic, permits a certain amount of vision within the instrument, can be obtained readily in slabs of almost any reasonable size, and can be readily worked if care is used.

The fixed coils and the damping box are each split into two halves in a vertical plane, each half being mounted in a rectangular glass panel.

These glass panels are hinged to each other, one being stationary and the other opening and closing like a door. In the closed position the corresponding halves of the fixed coils and the two halves of the damping box fit snugly together to form two complete fixed coils and one damping box.

The difficulty of attaching hinges directly to the glass forced the use of supporting frames of mahogany for the two glass panels. The hinges are attached to these frames. These frames also allow the lack of squareness of the corners of the glass panels to be corrected for and concealed. The use of any wood at all is an undoubted disadvantage. However, half of each fixed coil, half of the damping box, and the entire moving system are supported entirely by the stationary glass panel. The other half of the fixed-coil system and the other half of the damping box are supported by the second glass panel, which is attached to the first panel by the hinges and the mahogany frame. Any warping of the wooden frames can result only in a displacement of the entire second panel with respect to the first panel. The possibility of warping was reduced to a minimum by carefully varnishing the mahogany inside and out.

In order to provide an immediate and visible check on any gross misalinement of the two glass panels with respect to each other, two groups of fiducial marks were etched on the panels. Those groups were placed at widely separated intervals on the panels. Each group consists of a large cross etched on the rear surface of the rear panel, a smaller cross on the rear surface of the front panel, and a still smaller cross on the front surface of the front panel. With the instrument as originally assembled, the panels properly alined and the moving system free from sticking, the three crosses constituting each group lie accurately on a straight line perpendicular to the face of the panels. They may therefore be lined up by eye so as to fall one upon the other. Any subsequent displacement of one of the panels with respect to the other will be evident as a displacement of these fiducial marks from a straight line. It will be possible to bring the panels back into their original alinement by inserting suitable shims between the glass panels and the wooden frames.

The glass panels were made of plate glass of rectangular shape, 1 in. thick and 8 in. wide by 44 in. long. The only machine work required was to cut the glass to size and drill holes through it for mounting the wattmeter parts. Round holes are readily put through glass by using a tubular tool in a drill press with carborundum and water as a grinding compound. Holes of other shapes can be made by drilling a series of small round holes around the outline desired and then smoothing down the edges with a flat brass tool worked by hand with carborundum. The only prerequisite in working this glass was found to be patience. The location and size of the holes drilled in the glass panels are shown on the assembly drawing of the wattmeter in figure 1.

The fixed coils were mounted on the glass panels by first embedding them in bakelite holders which could be inserted into round holes in the glass panels. An attempt was made to mold the fixed coils into the Bakelite holders under heat and pressure by constructing a die which was used in a vulcanizing press. The heat and pressure of the press destroyed the insulation of the coils and the attempt had to be abandoned. The die was remade for molding cylindrically shaped

coil holders closed at one end. The fixed coils were cemented into these holders with sealing wax. Coils thus made have been in service 5 years now and still appear to be very solid. The coils in their holders were fixed in the glass panels with fiber shims pressed and cemented in place with a cellulose-acetate cement. The Bakelite holders were slightly smaller than the holes, and the holes in the glass were slightly conical to permit this construction. In constructing another instrument it might be desirable to make the holes even more conical deliberately for this purpose.

The damping box was made of molded Bakelite. It was molded in two pieces, the same die being used for each piece. Each half of the damping box fits into an opening in the bottom of each glass panel, as is shown in figure 1, and was fixed firmly in position by small wedges cemented in place. An opening was also made in the upper half of the movable glass panel to allow the free passage of a beam of light to and from the mirror attached to the moving system. The trim surrounding this opening was also made of molded Bakelite. A thin piece of cover glass, cemented on the rear surface of this piece of trim, allows the passage of light but protects the interior of the instrument from the stray air currents of the room.

(b) FIXED COILS

To obtain a high sensitivity for the completed instrument, the flux density at the moving coils, due to current flowing through the fixed coils, should be as great as possible. This would require a maximum number of ampere turns concentrated in a small space as a fixed coil. A limit as to the size of wire for the fixed coils, and thus to the allowable current flow through the instrument, is set by the introduction of eddy currents and skin effects in the larger sizes of wire. Number 16 copper wire, for which eddy currents and skin effects are negligible at power frequencies, was used in winding the fixed coils. A limit to the number of turns in the fixed coils is set by the introduction of capacitance currents. To keep these capacitance currents low, and to obtain some flexibility in current rating, four No. 16 silk-enamel copper wires were formed into a cable. These cables were then wound into tight coils (32 turns of cable per coil) on a coil-winding machine. A piece of fiber tubing, turned to the correct inside diameter, was slipped over the coil after completion of the winding; the coil and tubing were lashed together and repeatedly soaked in insulating varnish and baked. After the final baking, the fiber tubing was stripped from the coil and the coil mounted in the molded coil holders previously mentioned, with the aid of sealing wax. These coil holders were in turn mounted in the glass panels as previously indicated (see fig. 1).

Two different types of fixed coil were made (see fig. 2 for the shape and dimensions of each style of coil). Tests on the completed wattmeter showed that style *B* gave the better performance, and coils of this style are permanently mounted on the glass panels.

Four of these coils are required for the completed instrument, two mounted in each glass panel in such a manner that with the panels closed and face to face two complete fixed coils are formed, one above the other. Sufficient space is left to allow a moving coil to be suspended in the center of each of the two fixed coils so formed. The cables of the four individual coils were connected in series in such a manner that the flux of the upper coil is in the direction opposite

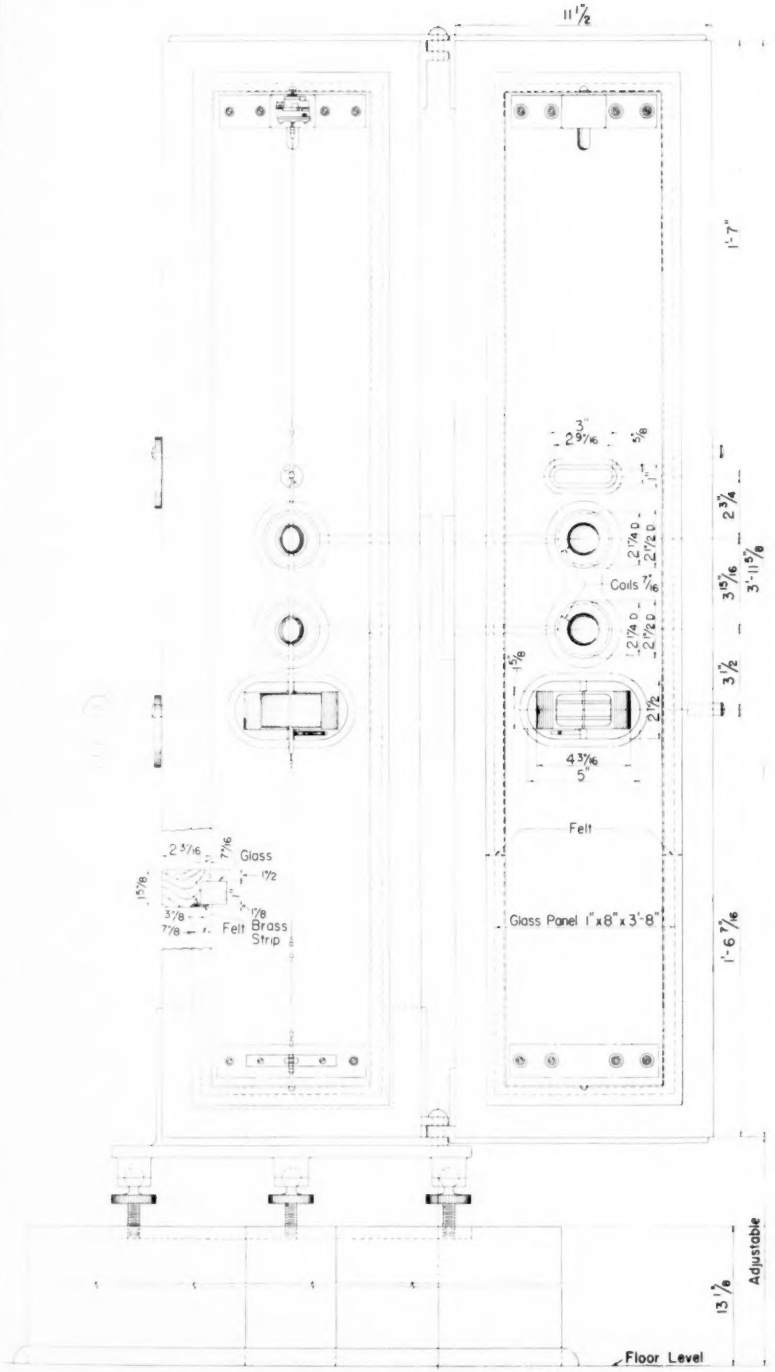


FIGURE 1.—*Drawing of the complete wattmeter, with front panel open.*

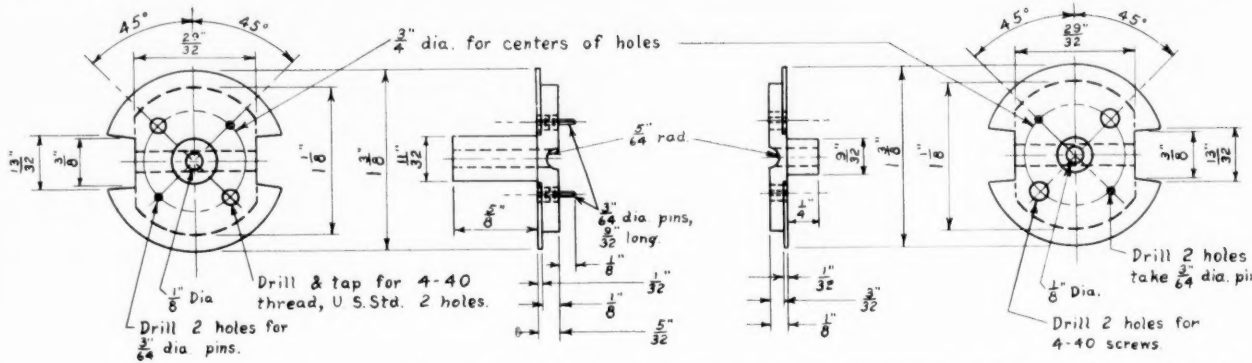
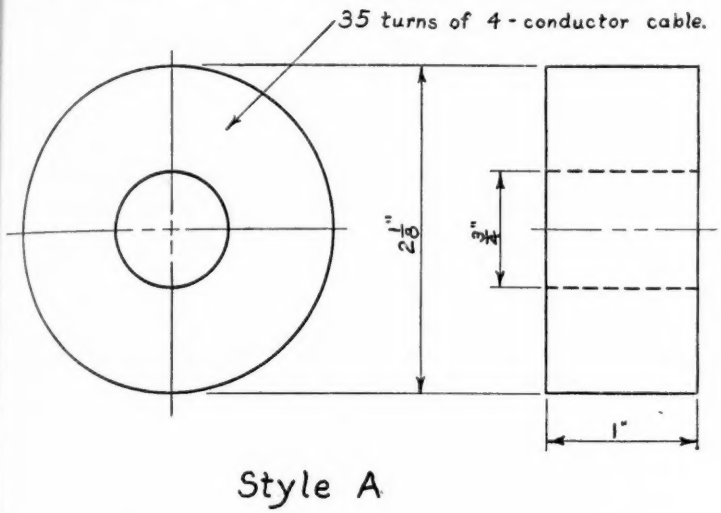

45°
45°
29/32"
3/4" dia. for centers of holes
5/64" rad.
3/64" dia. pins, 2/32" long.
Drill & tap for 4-40 thread, U S.Std. 2 holes.
1/8" Dia
Drill 2 holes for 3/64" dia. pins.
Drill 2 holes to take 3/64" dia. pins.
1/8" Dia.
Drill 2 holes for 4-40 screws.

FIGURE 4.—*The dimensions of the forms used for winding style B moving coils, which were permanently mounted in the completed instrument.*

Forms for style *A* coils were similar except that the outside diameter of the winding channel was 13/16 inch.

to the flux of the lower coil, thus giving astatic construction. The two ends of the fixed-coil cable were brought out to a terminal board located on the wall near the wattmeter. The terminal board is arranged so that the four coils formed by the four wires in the fixed coil cable can be connected in series, series-parallel, or parallel.



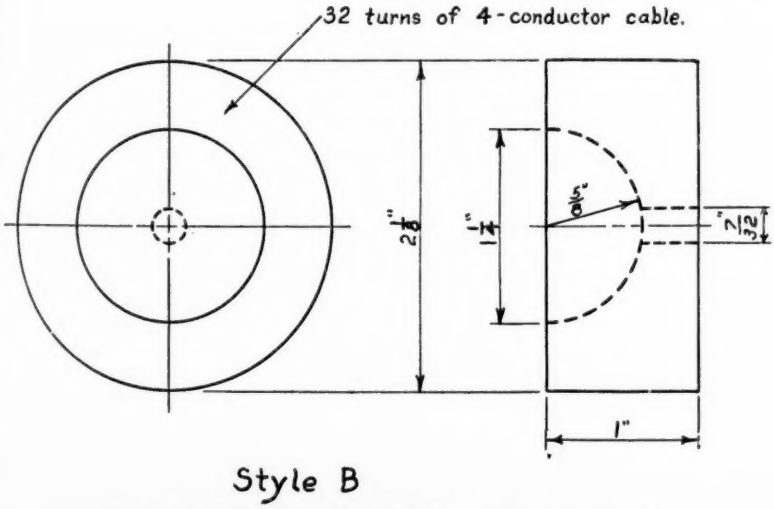


FIGURE 2.— *The dimensions of the two styles of fixed coils.*

Style *B* coils were permanently mounted in the wattmeter.

The current rating of the instrument is limited by the heating of the fixed coils. Each wire of the fixed-coil cable has a resistance of 0.25 ohm. Experimental heating runs were made with the fixed coils mounted in their working positions and with 2.5 amperes flowing in each wire of the fixed-coil cable. Under these conditions the fixed-coil system experienced a temperature rise of about 10°C when the current had been flowing for about 2½ hours. Previous experience has indicated that the position of the moving coils becomes uncertain, because of convection currents in the air, if the temperature rise in the fixed coils is much more than 10°C. The current rating of the fixed coils has therefore been set at 2.5 amp with the four wires in series, 5 amp with the four wires in series-parallel, and 10 amp with the four wires in parallel. These current ratings are conservative on a self-heating basis and might be exceeded by moderate amounts with some sacrifice in accuracy if necessary.

(c) MOVING SYSTEM

In order to provide a rigid connection between the various parts of the moving system,[5] all the components of the moving system are mounted on a stiff Bakelite tube, 3/16 in. in outside diameter and 13½ in. long. This tube is suspended in a vertical position by means of two phosphor-bronze suspension ribbons. These ribbons, 1.5 mils thick and 20 mils wide, are mechanically attached to the tube by means of special brass and aluminum chucks fastened on the ends of the tube. The shank of each chuck is so milled as to allow the suspensions to come through under the shell. Thus the moving coil can be soldered directly to the end of the ribbon to form a definite electric contact, and the chuck jaws make a definite mechanical connection on a portion of the suspension which has not been softened by heating with a soldering iron. This construction minimizes zero shift and the failure of soldered joints in the moving system.

The upper suspension ribbon extends 12 in. above the chuck on the top end of the Bakelite tube, and there it is fastened to a similar chuck which is supported by an adjustable head attached to the top of the stationary glass panel. This head is so built that the chuck attached to it can be moved independently along any one of the three coordinate axes and can also be rotated about the vertical axis. The mechanism of this adjustable head is shown in figure 3.

The lower suspension ribbon extends 8 in. below the chuck on the bottom end of the Bakelite tube, and there it is coupled by means of a double-end chuck, similar to those already described, to the top of a phosphor-bronze coil spring. The bottom of this coil spring is attached to another chuck which is supported from the bottom of the stationary glass panel by means of a machine screw that allows a vertical adjustment for setting the tension on the suspension. This tension is adjusted to about 230 g, but the wattmeter performance is not greatly affected by changes in this value.

In order to make the mechanical zero of the instrument relatively insensitive to small alterations in the leveling of the instrument, it is

[5] If the entire moving system is not rigidly interconnected, it is possible, particularly at very low power factors, for forced internal vibrations to take place between its component parts. The result is a broadening of the reflected spot of light. Because of the varying scale law of the instrument, particularly if the moving coils are not at the position of zero mutual, the true position of the spot of light will not correspond to the midpoint of this broadened band of light. The apparent indication of the instrument will therefore be in error.

desirable to have the center of mass of the moving system coincide with the line of suspension of the moving system. Weights for balancing the moving system are therefore attached to the Bakelite support rod by the use of a brass collar with three small threaded rods (120 degrees apart) projecting from the collar. The balancing weights consist of small thumb nuts fitting these threaded rods.

Two sizes of moving coils were made originally, one with a 13/16-in. outside diameter to fit style *A* fixed coils, and the other with a 1$\frac{3}{16}$ in. outside diameter to fit style *B* fixed coils. Because of the greater sensitivity of the wattmeter with this latter combination, as explained in section d, Preliminary Tests of Wattmeter, style *B* fixed coils and

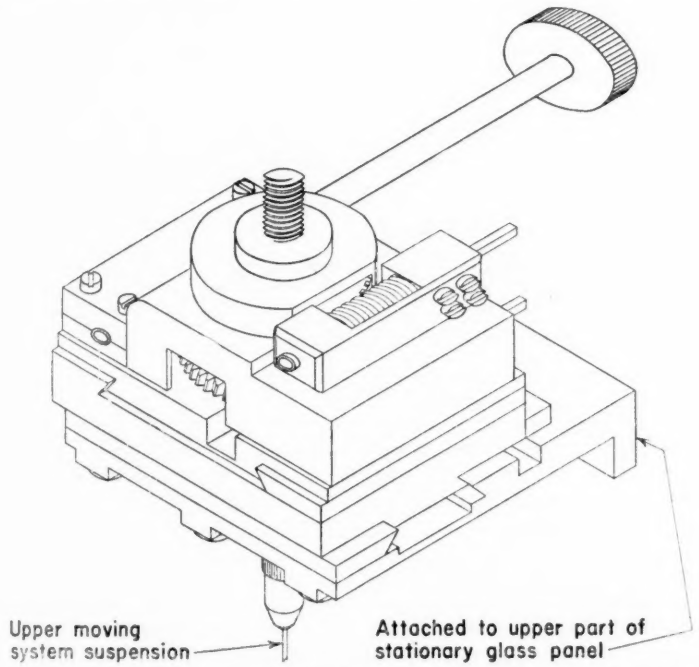


FIGURE 3.—*Details of the movable head to which the upper end of the suspension is attached.*

the larger moving coils were chosen for permanent mounting in the wattmeter.

The details and dimensions of the brass forms used for winding these coils are given in figure 4. Each coil contains 100.5 turns of No. 32 silk-enamel copper wire. After each layer of a coil was wound (about 19 turns), a coat of thin shellac was applied and allowed to dry. This served to hold the completed coil together after removing the form. The completed coil was then dipped in thin insulating varnish and baked at about 120°C for 24 hours. This procedure was repeated four times to form a tough protective coating over the coil and to give it rigidity. The coils were mounted on the moving system by inserting the suspension tube through the two holes in the

top and bottom of the coil. After the moving coils were located on the tube so as to fit into the hollow centers of the fixed coils and the two moving coils were twisted into the same plane, they were lashed to the tube with silk thread and shellac was applied to hold them rigidly to the tube. The two moving coils were connected in series in such a manner that the direction of winding on the upper coil is reversed with respect to the direction of winding on the lower coil. The two remaining free ends of the coils were then soldered to the upper and lower suspensions.

The damping vane, 1½ in. high by 4 in. wide, is made of 10-mil sheet aluminum with the edges rolled for stiffness. This damping vane is riveted to the suspension tube at the proper distance below the lower moving coil to fit into the damping box when the moving system is in place.

Two mirrors are attached to the suspension tube above the upper moving coil by the use of brass collars and spiders. One mirror (⅜ in. in diameter) is located so that with the moving coils in the position of zero mutual inductance with the fixed coils it reflects a beam of light from a straight filament lamp onto the center of a 50-cm ground-glass scale located 2 m directly in front of the wattmeter. The other mirror (¼ in. in diameter) is located on the tube so that its plane makes an angle of 60 degrees with the plane of the first mirror. The mechanical zero of the moving system is normally set so that the lightbeam reflected from this smaller mirror falls on the center of the ground-glass scale when the instrument circuits are open. This allows any shifts in the mechanical zero to be readily detected.

(d) PRELIMINARY TESTS

Before designing a series resistor for the voltage circuit of the wattmeter, it was necessary to know the maximum allowable moving-coil current and the wattmeter sensitivity. The wattmeter was therefore set up in its operating position and the optical system adjusted until the spot of light from the ⅜-in. mirror fell on the center of the ground-glass scale when the moving coils were in their position of zero mutual inductance with the fixed coils. The position of zero mutual inductance is readily determined by passing an alternating current through the fixed coils and shorting across the moving-coil terminals. If the moving coils are in the zero mutual position, there will be no deflection of the moving system. If they are not at the position of zero mutual, there will be an emf induced in them and a current will flow when their terminals are shorted, causing a deflection towards the position of zero mutual. This test can be made as sensitive as desired by increasing the frequency of the current in the fixed coils.

A preliminary value of the sensitivity of the wattmeter with the moving coils in the position of zero mutual was determined by passing rated direct current (2.5 amp per wire) through the fixed coils and measuring the direct current through the moving coils necessary to obtain a deflection of about 10 cm with a scale distance of 2 m. The sensitivity with style *A* fixed coils and the smaller moving coils was found to be 34 cm/ma in the moving coil. The sensitivity for style *B* fixed coils and the larger moving coils was found to be 125 cm/ma in the moving coils. These latter were therefore permanently mounted in the instrument. This latter sensitivity might alternatively be

expressed as 2.4 milliradians per ampere turn in the fixed system per ampere turn in the moving system.

The maximum allowable current through the moving coils is limited by the heating due to this current. A heating test was made with 2.5 amp through the fixed coils (all connected in series) and 0.1 amp through the moving coils. Under these conditions the moving coils showed a temperature rise of 9.5° C at the end of 2½ hours. A current of 0.1 amp is therefore considered a safe value for the moving system. Higher current values might be used, but their use is not anticipated at this time.

(c) SERIES RESISTOR

The resistors to be used with the moving coils of this instrument to form the voltage circuit were designed to be adjustable over such a range that by means of this adjustment the instrument deflection could be brought to the same value for any nominal value of watts to be measured. A total deflection of 400 cm was chosen, thus allowing a change in deflection of 0.01 percent (0.4 mm) to be observed easily. With a sensitivity of 125 cm/ma in the moving coils for rated current in the fixed coils, a plain series resistor must have a maximum resistance of 337 ohms per volt; that is, about 100,000 ohms for the maximum voltage range of 300 v. The minimum fixed-coil current (with fixed coils connected in series) at which the wattmeter is expected to be used is 0.25 amp (25-percent load on the 1-amp range of a watthour meter). This requires a maximum moving-coil current of 0.03 amp to obtain a deflection of 400 cm. It was decided to design the resistor for a maximum current of 0.06 amp and to provide a circuit arrangement which would give a moving-coil current equivalent to that which would be obtained if a plain series resistor were used with a maximum resistance of 200,000 ohms.

The arrangement of resistors and their electric connections designed to meet these requirements is shown in figure 5. A fixed resistance of 985 ohms is connected in series with the wattmeter moving coil, and a capacitance of 0.001 microfarad is connected across a 937-ohm section of this resistor to compensate for the inductance of the moving coils. The "series resistance" consists of nine 1-ohm, nine 10-ohm, nine 100-ohm, and nine 1,000-ohm coils connected to four 10-step selector switches so that any resistance from zero to 9,999 ohms, in 1-ohm steps, may be connected. The "shunt resistance" is connected in parallel with the moving coil and the 985-ohm resistor. The value of this shunt resistance may be set at ∞, 1,000, 400, 200, 100, or 50 ohms by means of a 6-step selector switch. The purpose of the shunt resistance is to decrease the current through the moving coil, which, as regards voltage sensitivity, is the equivalent of increasing the series resistance. This allows an effective series resistance of 200,000 ohms to be attained while the actual value of the series resistor is kept below 10,000 ohms. The coils used in the shunt resistance (1,000 ohms and lower) are much cheaper and less apt to give trouble than the 10,000-ohm coils that would be needed in the series resistance if a shunt resistance were not used. In addition the capacitance errors of the 1,000-ohm coils will be much less than the capacitance errors of 10,000-ohm coils.

A 1-μf paper capacitor can be connected across the 985-ohm resistance which is in series with the wattmeter moving coils by means of the push-button switch marked "P. F. test." When this capacitor is

connected, the current through the moving coils is made to lead in phase with respect to the supply voltage. Thus, if the current supplied to the wattmeter fixed coils is lagging in phase with respect to the supply voltage, pushing the "P. F. test" button will cause the

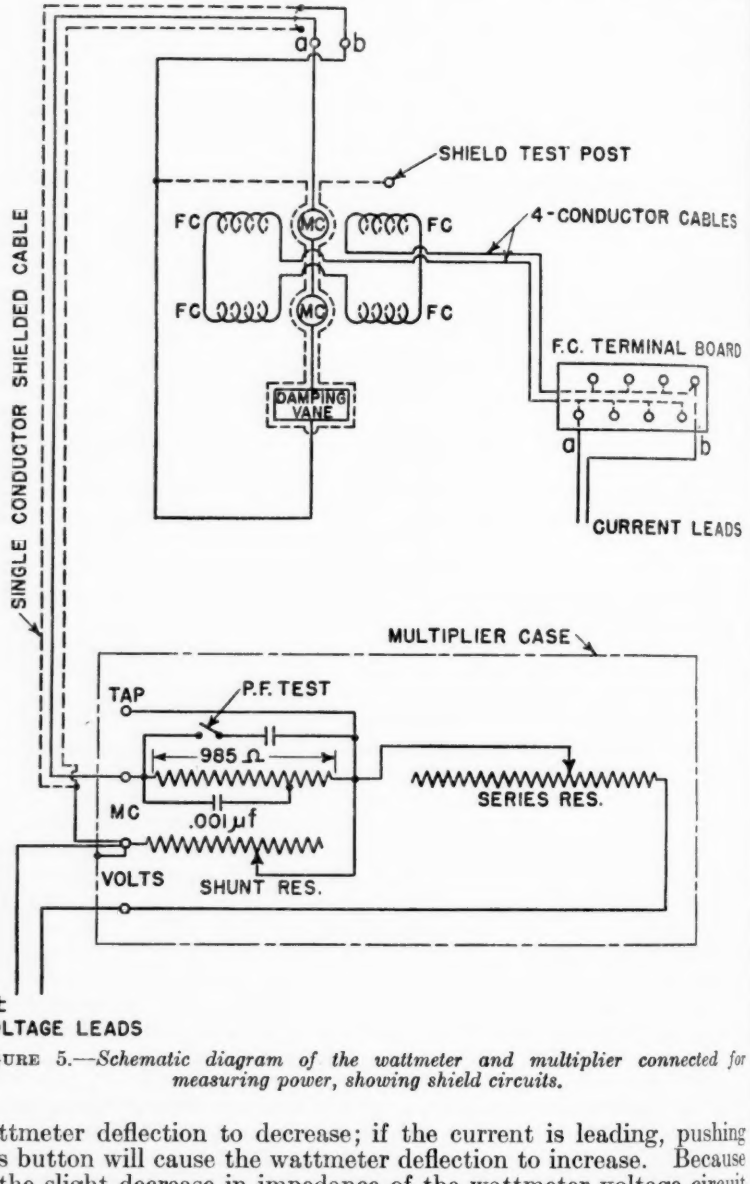


FIGURE 5.—*Schematic diagram of the wattmeter and multiplier connected for measuring power, showing shield circuits.*

wattmeter deflection to decrease; if the current is leading, pushing this button will cause the wattmeter deflection to increase. Because of the slight decrease in impedance of the wattmeter voltage circuit when the 1-μf capacitor is connected, this "leading" or "lagging" test is ambiguous when the power factor is greater than 0.9.

The resistance units used in this multiplier are all of commercial construction, except an 85-ohm section of the 985-ohm resistor connected in series with the moving coils. This 85-ohm resistor was made in this laboratory. It is of bifilar construction in two sections, allowing a tap to be brought out at the proper point for connecting the 0.001-μf compensating capacitor. The 1- and 10-ohm units are also of bifilar construction. All other units were of a special "woven" construction which reduces the time constant to the lowest value attainable for precision resistors. They are mounted on porcelain tubes ⅞ in. in diameter and 3½ in. long and then dipped in "Ceresin" wax. The units are all made of manganin wire, and with a current of 60 ma their maximum temperature rise was specified to be less than 25° C. In order to obtain this current rating, the 1,000-ohm units are each made up of four 4,000-ohm windings mounted on separate spools and connected in parallel.

All the component parts of the multiplier are mounted on a hard-rubber panel ½ by 11½ by 20½ in. This hard-rubber subpanel is concealed from exposure to light by an aluminum panel ⅛-in. thick placed ½ in. in front of it and attached to it by brass screws and hard-rubber spacers. The shafts of the selector switches and the binding posts protrude through the aluminum panel without touching it. These two panels are screwed to an aluminum base ¼ by 5 by 20½ in. A one-piece brass cover is bent up to fit over the top, back, and two sides. The completed multiplier box is fastened in an upright position at the back of the observer's table, the ground-glass scale being located 5 in. in front and 3 in. above it.

(f) SHIELDING

In order to minimize the effect of capacitance currents between the moving and fixed coils and to prevent the accumulation of electrostatic charges near the moving coils or damping vane, it is usual to provide a conducting screen or shield between the fixed and moving parts. In the present instrument conducting paint was used in making this shield. Four ⅛-in. stripes are painted along the axes of great circles on the inside of the hemispherical depression in each fixed coil so that they cross each other at the deepest point in the depression. The inside surface of each half of the damping box is coated with this paint, the glass windows being left clear except for two ⅛-in. stripes painted across them. All sections of the shield are connected in series by a ⅛-in. stripe of conducting paint, the connection from the stationary glass panel to the hinged panel being made by a spring contact between the two halves of the damping box. One end of this series circuit is connected to the moving-coil lead going to the bottom suspension (the damping vane is soldered to the lead from this suspension to the lower moving coil). The other end of the series circuit is brought out to a binding post on the mahogany frame of the hinged panel. A measurement of the resistance between this binding post and a moving-coil terminal thus serves as a check on the continuity of the shield. This resistance as measured by a 1½-v ohmmeter is about 50,000 ohms.

A schematic diagram of the location and interconnection of the shields used in the instrument is shown in figure 5. The wattmeter moving coil is connected to the multiplier by a single-conductor

shielded lead with rubber insulation over the shield (the capacitance between conductor and shield being 710 $\mu\mu$f). At the wattmeter end, the shield of this lead is connected through a binding post to the lower moving-coil suspension, which is also tied to the wattmeter shield. The central wire of this lead is connected through a binding post to the upper moving-coil suspension. At the multiplier end, the shield of this lead is connected to the lower moving-coil "MC" binding post (the "$\pm$" supply voltage lead to which the electrostatic tie between current and voltage circuits is attached is also connected to this binding post). The central wire of the shielded lead is connected to the upper moving-coil binding post. The multiplier metal case is tied to the lower moving-coil binding post and thus acts as a shield for the multiplier.

(g) WATTMETER CONSTANTS

(1) *Fixed coils.*

1. Connected in series (2.5 amp), resistance 0.848 ohm, self inductance 1,300 μh.
2. Connected in series-parallel (5 amp), resistance 0.212 ohm, self inductance 304 μh.
3. Connected in parallel (10 amp), resistance 0.053 ohm, self inductance 72 μh.
4. Mutual inductance between any two of the four fixed coils, 85 μh.
5. Average capacitance between two of the four fixed coils, 0.003 μf.
6. Capacitance from fixed coils to shield, 200 $\mu\mu$f.
7. Maximum heating of fixed coils with rated current, 10° C.
8. Flux density at moving coils with rated current flowing in fixed coils, 110 gauss.

(2) *Moving system.*

1. Resistance of single moving coil, 5.3 ohms.
2. Resistance of entire moving system (between terminals on back of wattmeter), 15.30 ohms.
3. Self inductance of moving system, 830 μh.
4. Mutual inductance between fixed coils (connected in series-parallel) and moving coils at position of mechanical zero (58 degrees from position of zero mutual inductance between fixed and moving coils), 135 μh.
5. Capacitance between moving system and shield, 52 $\mu\mu$f.
6. Capacitance between moving system and fixed coils (with shield at same potential as moving system), 9$\mu\mu$f.
7. Maximum heating of moving coils with 0.1 amp flowing through them and rated current through fixed coils, 10° C.
8. Total weight of moving system, 18 g.
9. Period of moving system, 8 sec.
10. Torque required to deflect moving system from mechanical zero to full scale (position of zero mutual), 30 dyne cm.
11. Stiffness of suspension, 0.5 dyne cm/deg.
12. Natural frequency of internal resonance; with direct current on fixed coils and alternating current on moving coils maximum vibration occurs at 80 c/s.

III. PERFORMANCE TESTS

1. DIRECT-CURRENT ACCURACY

Before the ac-dc errors were determined, the accuracy of the instrument assuming no ac-dc errors, that is d-c accuracy, was investigated. The factors effecting the d-c accuracy are (1) drift of deflection with time for a constant value of power, (2) variation of wattmeter sensitivity for small changes in deflection, and (3) imperfection of astatic construction.

With a constant value of current in the fixed coils and a constant voltage across the moving-coil circuit, the deflection of the wattmeter was noted during a period of 2 hours. The drift in deflection was found to be very nearly a linear function of time and equal to 0.1 mm/min. In ac-dc transfer tests the effect of this drift is cancelled in the average a-c and d-c readings by the sequence in which the readings are taken. When the instrument is used as a standard wattmeter, it is calibrated on direct current before and after the a-c readings are taken so that here also the effects of drift tend to cancel. Even if the drift were not cancelled by the sequence of taking readings, the maximum error caused by it would be only 0.025 percent in 10 minutes.

In an ac-dc transfer test of a wattmeter that is neither magnetically shielded nor of astatic construction, the reading of the standard instrument may be several percent different for one direction of current and voltage than for the reversed direction; also, the a-c reading may be slightly different from the d-c readings. Since the scale of the standard instrument is uniform, if its sensitivity is different for the various readings of the standard instrument in one set of data, an error will be introduced which may be as large as the percentage difference in sensitivity.

The sensitivity of the wattmeter can be derived from the following quantities:

G=torque on moving system in dyne-centimeters per milliampere in the moving coils with rated current in the fixed coils.

α=angular deflection of moving system from the mechanical zero position as measured by the travel in centimeters of the working spot of light at a 2-m radius from the mirror.

U=restoring torque of suspension in dyne-centimeters per unit of angular deflection, α.

i=moving-coil current in milliamperes.

Since the summation of the torques on the moving system is zero, for any fixed position of the moving system

$$iG-\alpha U=0 \text{ or } \alpha=i\frac{G}{U},$$

that is, the wattmeter sensitivity as deflection in centimeters per milliampere in the moving coils is G divided by U. From Hooke's Law U is constant but

$$G=K\frac{dM}{d\alpha},$$

where M is the mutual inductance between the moving and fixed coils. Thus sensitivity is a function of the position of the moving coils with respect to the fixed coils but is independent of the mechanical zero or total deflection of the moving system.

The true value of sensitivity is obtained by measuring α for a given value of i and dividing α by i. In the present wattmeter with a 50-cm scale and a total normal deflection from mechanical zero position of 400 cm, it is not feasible to obtain an accurate value of α at normal deflection. However, the changes in α over the range of the 50-cm scale can be accurately measured, and if the total deflection is known to a fairly close approximation for one point on the scale, the changes in sensitivity on the scale can be accurately determined.

The values of relative sensitivity (which are absolute values within 0.3 percent and which show changes in sensitivity over the scale range within 0.01 percent) were obtained by holding rated current through the fixed coils and measuring the moving-coil currents required to deflect the moving system from the normal mechanical zero position (beam of light from small mirror on center of scale) to various positions of the working spot on the scale at 5-cm intervals. Since the sensitivity is very nearly constant at the point of zero mutual inductance, a reference value of sensitivity at this point was computed from the values of α and i at points 5 cm to the right and left of this point, that is,

$$\alpha_R=\frac{G_0}{U}i_R \qquad \alpha_L=\frac{G_0}{U}i_L,$$

from which

$$\frac{G_0}{U}=\frac{\alpha_R-\alpha_L}{i_R-i_L}$$

and the total deflection at the point of zero mutual inductance is

$$\alpha_0=\frac{G_0}{U}i_0.$$

The total deflection at any other point on the scale was found by adding the difference between the scale reading at this point and the scale reading at the point of zero mutual to the total deflection at the point of zero mutual. This gave total relative deflections for various points on the scale which were as accurate as the scale could be read.

From these data the relative wattmeter sensitivity at any point on the scale was computed by dividing the total deflection at the point by the moving-coil current required to deflect the wattmeter to this point. The relative sensitivity this obtained is in deflection (in centimeters) per milliampere in the moving coils with rated current in the fixed coils. A plot of this sensitivity against scale reading is shown in figure 6. This plot shows that there is a range of 10 cm near the point of zero mutual within which the sensitivity is constant to within 0.01 percent. Thus no corrections for wattmeter sensitivity are required for readings within this range. For readings outside this range corrections [6] can be applied.

As seen from the curve of figure 6, the point of zero mutual inductance between the fixed and moving coils (as indicated by the arrow)

[6] For a computation of these corrections see appendix I.

does not exactly coincide with the point of maximum sensitivity. If the flux density due to the fixed coils were uniform throughout the volume occupied by the moving coils, maximum sensitivity, that is maximum $dM/d\alpha$, would come at the point where $M=0$. The con-

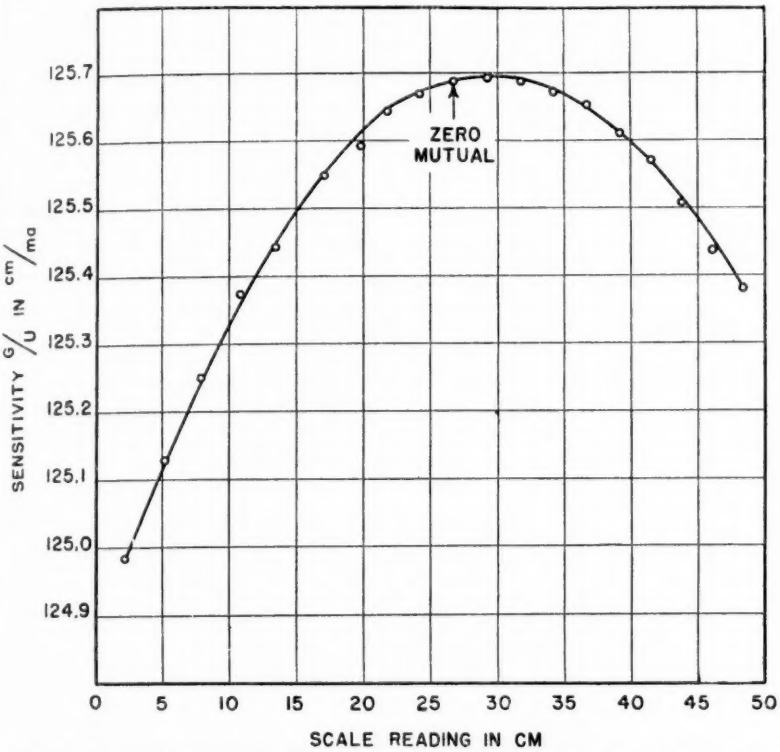


FIGURE 6.—*Relative wattmeter sensitivity for various positions of working spot on the ground-glass scale in centimeters of deflections per milliampere in the moving coils with rated current in the fixed coils.*

The absolute wattmeter sensitivity is equal to the relative sensitivity to within 0.3 percent.

clusion is that the flux density is not strictly uniform in the present instrument, and this is probably the case in most instruments of this type.

Imperfection of the astatic construction of the wattmeter results in a small deflection of the moving system with direct current through the moving coils only, because of interaction with the earth's magnetic field. This deflection was measured with 60 ma (the maximum value to be used) through the moving coils for various positions of the moving system near the point of zero mutual inductance between the fixed and moving coils. These deflections as measured by the movement of the light beam on the ground-glass scale were found to be $+0.07$ cm for one direction of moving-coil current and -0.07 cm for the other direction, and they were the same for all positions of the light beam on the scale within ± 15 cm of the point of zero mutual inductance. Thus in using the instrument for an ac-dc transfer test, even though

the two d-c readings are quite different, the small deflection due to lack of astaticism will be cancelled out in the average d-c reading.

2. ANALYSIS OF AC-DC ERRORS

The present instrument was found to have ample sensitivity and its errors on direct current, as explained above, were not greater than 0.01 percent. However, this instrument was intended for use as an ac-dc transfer instrument and for this purpose its deflection for a given value of power must be the same on alternating current as on direct current. Before devising the actual tests for determining the ac-dc errors, it is advisable to analyze the various sources of such errors. They may be listed as follows:

1. Interaction between moving coils and other parts of the voltage circuit.
2. Magnetic impurities in the moving system.
3. Induced and capacitance currents in the moving system.
4. Eddy current or skin effects in the fixed coils.
5. Capacitance currents in the fixed coils.
6. Phase defect in the voltage circuit.[7]

The average deflection of a wattmeter for direct and reversed directions of a given direct voltage, E_d, across its moving-coil circuit and a given direct current, I_d, through its fixed coils may be expressed as

$$\alpha_d = KE_dI_d.$$

If the direct current and voltage are replaced by an alternating current, I_a, and an alternating voltage, E_a, such that $E_aI_a \cos \Theta = E_dI_d$, were E_a and I_a are simple sine functions of time and Θ is the angle of lag of I_a with respect to E_a, and if the wattmeter is free of ac-dc errors, the deflection on alternating current would be

$$\alpha_a = KE_aI_a \cos \Theta = KE_dI_d = \alpha_d.$$

However, as noted above, there are a number of possible sources of ac-dc errors and these errors enter into the above equation as (1) "Δm", a percentage change in magnitude of E_aI_a, (2) "τ_w", in effect, a change in the angle Θ, and (3) "$\Delta\alpha$", a change in α_a, which is a function of I_a or E_a but not of the product E_aI_a. When these three factors are put into the equation, the deflection on alternating current becomes

$$\alpha'_a = KE_aI_a(1+\Delta m) \cos (\Theta+\tau_w)+\Delta\alpha.$$

and the difference between the average d-c deflection and the a-c deflection is

$$\alpha'_a - \alpha_a = \Delta m KE_aI_a \cos \Theta - KE_aI_a \sin \Theta \sin \tau_w + \Delta\alpha \qquad (1)$$

neglecting second-order terms.

The sources of ac-dc error listed above may now be separated into three groups according to their entrance in eq 1 as "Δm", "τ_w", or

[7] In uncompensated electrodynamic instruments the largest source of this phase defect is the inductance of the moving coils. In the present instrument this inductance is compensated by a capacitor connected across a section of the series resistor. Thus, this phase defect (difference in phase between the moving-coil current and the voltage across the voltage circuit) depends upon (1) the efficacy of the compensation, (2) the small residual inductance or capacitance in the series resistor, and (3) the small capacitance currents between various sections of the series resistor or from any of these sections to the multiplier case.

"$\Delta\alpha$". Those entering as "$\Delta\alpha$" will be present either with voltage only or with current only applied to the wattmeter, and by properly choosing the experimental conditions each one of these errors can be measured separately. The errors entering as "Δm" may be measured as a group by determining the ac-dc errors of the wattmeter at unity power factor (making $\sin\Theta=0$), and the errors entering as "τ_w" may be measured as a group by determining the ac-dc errors of the wattmeter at zero power factor (making $\cos\Theta=0$). The "$\Delta\alpha$" errors will also be present in measurements at unity and zero power factor; but since the "$\Delta\alpha$" errors can be determined independently, corrections can be applied for them.

3. ERRORS DEPENDING ON *E* OR *I* SEPARATELY—"$\Delta\alpha$"

(a) INTERACTION BETWEEN PARTS OF VOLTAGE CIRCUIT

If there were appreciable interaction between the moving coils and other parts of the voltage circuit, it would cause a deflection of the moving system when voltage only (either alternating current or direct current) is applied to the wattmeter. In order to detect this effect if present, 100 volts alternating current (a d-c voltage would cause a deflection by reaction with the earth's magnetic field as explained above) were applied to the voltage circuit. No deflections were observed for values of series resistor from 2,000 to 10,000 ohms, and it was concluded that this interaction effect is negligible.

(b) MAGNETIC IMPURITIES IN THE MOVING SYSTEM

Although the utmost care was exercised in selecting materials for and construction of the wattmeter moving system, there is a possibility that the resulting system may contain magnetic impurities. If the magnetic impurity is not symmetrically distributed around the moving-system axis, it will cause the moving system to deflect with current through the fixed coils only. With magnetic impurities, such as "hard iron" filings, which are capable of retaining some magnetism, the deflection of the moving system would not be the same for alternating current in the fixed coils as for direct current and in the case of direct current it would depend on the direction of the current. With magnetic impurities of zero retentivity, the deflection of the moving system would be the same for alternating current as for direct current through the fixed coils but would vary as the square of the magnitude of this current. In measuring a given value of watts, the alternating current will be different from the direct current if (1) the alternating and direct voltages are different or (2) the power factor is other than unity. Thus, even though the magnetic impurities have zero retentivity, the deflection caused by them will not necessarily be the same for equal magnitudes of a-c and d-c watts being measured.

When the present wattmeter was first assembled, one of the tests consisted in putting current through the fixed coils, the moving-coil circuit being open, and noting the deflection of the moving system. Deflections as large as 2 mm (0.05 percent of normal full-scale deflection) were observed. The magnitude of these deflections varied with the orientation of the moving system with respect to the fixed coils but was independent of the frequency of the current through the fixed coils, indicating that the deflections were caused by magnetic impurities in the moving system.

The component parts of the moving system (1, moving coils; 2, mirror; 3, collars and clamps for holding mirrors; 4, collar with adjustable weights for balancing the system; 5, damping vane; and 6, Bakelite tube upon which all other parts were mounted) were all made of materials that are normally considered to be nonmagnetic. With the moving system assembled it was impracticable to determine which of the component parts contained magnetic impurities. A new moving system was constructed and each component part was tested for magnetic impurities before assembly. This test consisted in suspending the part, with a small mirror attached to it for reflecting a beam of light onto a scale, in the field of a strong electromagnet and noting the deflection of the beam of light when the coil of the electromagnet was energized. These tests showed that a Bakelite tube, obtained from the same source as the tube used in the first moving system, contained considerable magnetic impurities which appeared to be concentrated in a plane containing the central axis of the tube. This would account for the results obtained with the first moving system in the wattmeter. In searching for a substitute for this tube, samples of glass, porcelain, clear Bakelite (no filler), and other resins were tested for magnetic impurities. It was found that these samples contained only very slight magnetic impurities in comparison with a sample of the Bakelite tube used in constructing the first moving system. Thus it was concluded that the filler used in making the Bakelite tube and not the Bakelite itself contained the magnetic impurity. Four samples of Bakelite tube were obtained from separate sources and tested for magnetic impurities. Of these four, one was chosen which contained about the same amount of magnetic impurity as the glass or porcelain, and a new moving system was constructed using a tube of this material for mounting the moving-system parts. Before mounting each component part on the new moving system, the system was suspended in the wattmeter and its deflection was noted with current through the fixed coils only. At each stage of construction this deflection was just barely noticeable with rated current through the fixed coils. When the moving system was completed, twice-rated current was passed through the fixed coils and measurable deflections of the moving system were obtained. The moving coils were then twisted around on the Bakelite tube until the position of zero mutual inductance between the fixed and moving coils (the position near which the moving coils are held when the wattmeter is in use) coincided with the position for minimum deflection of the moving system with current through the fixed coils only. The deflection of the moving system at this position was found to be about 0.2 mm (0.005 percent of normal wattmeter deflection) with twice-rated current through the fixed coils. Thus it was concluded that the error due to magnetic impurities would be negligible with rated current through the fixed coils.

c) INDUCED AND CAPACITANCE CURRENTS IN THE MOVING SYSTEM

The effects of induced and capacitance currents in the moving system increase as the frequency of the fixed-coil current is increased, and although they are entirely negligible at power frequencies (as shown in the tests made to detect magnetic impurities in the moving system) they may become measurable at frequencies above 1,000 c/s. They may be detected by passing high-frequency current through the

fixed coils with the moving coils open-circuited and noting any deflection of the moving system. When rated current at a frequency of 2,000 c/s was passed through the fixed coils, deflections of the moving system as large as 1 cm were obtained. These deflections are the result of a combination of the following effects: (1) eddy currents within the thickness of the wires forming the individual turns of the moving coils, (2) eddy currents in other parts of the moving system, such as the damping vane, and (3) capacitance currents flowing in some of the moving-coil turns and through the capacitance existing between the fixed and moving coils.

The summation of the torques produced by eddy currents in individual turns of the moving coils tends toward zero and would be exactly zero with the moving coils in the position of zero mutual inductance with the fixed coils if the fixed-coil flux were uniform throughout the area occupied by the moving coils. Any torque produced in the present wattmeter by the eddy currents in the moving coils may be combined with the torques produced by eddy currents in other moving parts of the wattmeter, since the torques due to all these eddy currents are similar functions of the same variables.

The three effects causing the deflections noted above may now be considered as two: (1) eddy currents in moving system, and (2) capacitance currents flowing in some of the moving-coil turns. The deflection due to eddy currents will (a) increase approximately as the square of the frequency of the fixed-coil current, (b) increase as the square of the current through the fixed coils; but it will be independent of (a) the efficacy of the shield between the fixed and moving coils, (b) the location of the electrostatic tie between the fixed and moving coils, and (c) the connection of the fixed coils (series, series-parallel, or parallel). The deflection due to capacitance currents will (a) increase approximately as the square of the frequency of the fixed-coil current, (b) increase as the square of the current through the fixed coils, (c) depend upon the efficacy of the shield between the fixed and moving coils, (d) be approximately unchanged in magnitude but reversed in direction when the electrostatic tie between fixed and moving coils is changed from one terminal of the fixed coils to the other terminal, and (e) depend upon the fixed-coil connections, being largest for series and least for parallel. The total deflection caused by eddy currents and capacitance currents may be separated into its two components by use of relation (d). For a given magnitude and frequency of fixed-coil current the deflection of the moving system was noted with (1) the $\pm$ or b terminal of the moving coils connected to terminal a (see fig. 5) of the fixed coils, (2) the b terminal of the moving coils connected to terminal b of the fixed coils. The algebraic mean of these two deflections is the deflection caused by eddy currents, and one-half the algebraic difference between these two deflections is the deflection caused by capacitance currents.

From tests performed on the wattmeter with rated current at a frequency of 2,000 c/s through the fixed coils, the deflections due to eddy currents in the moving system and capacity currents in the moving coils were determined and the results are shown in table 1. These tests were performed with the shield between the fixed and moving coils tied to the $\pm$ side of the moving-coil circuit as shown in figure 5. With this shield "floating," the deflections due to capacitance currents were found to be about three times those given in the table.

TABLE 1.—*Wattmeter deflections due to eddy currents and capacity currents*

[Moving-coil circuit opened. Fixed-coil current frequency, 2,000 cycles. Shield tied to moving coil terminal *b*.]

Fixed coil-connections	I_c	MC terminal *b* tied to	Total wattmeter deflection	Deflection due to eddy currents	Deflection due to capacitance currents
	amp		*cm*	*cm*	*cm*
Series	2.5	FC *a*	0.47	0.76	0.28
		FC *b*	1.04		
Series-parallel	5	FC *a*	0.50	.68	.18
		FC *b*	.86		
Parallel	10	FC *a*	.56	.66	.09
		FC *b*	.75		

The deflection of about 0.70 cm given in table 1 as due to eddy currents in the moving system seemed quite large. In order to determine which part of the moving system contained these eddy currents, a coil was placed near the wattmeter in such a position that, with a given value of current at 2,000 c/s passing through this coil, the magnetic field strength at the damping vane would be about the same as that produced by the wattmeter fixed coils at rated current and the magnetic field strength at other parts of the moving system would be low. With current flowing through this external coil and no current through the wattmeter coils, the deflection of the moving system was found to be about 0.50 cm. Thus it appears that most of the deflection due to eddy currents in the moving system is caused by eddy currents in the damping vane. In constructing another wattmeter, it would be advisable either to increase the distance between the damping vane and wattmeter coils or to use as a damping vane some nonconducting material, coated with a very thin conducting film to eliminate accumulation of static charge.

Another possible source of induced currents in the moving system is the mutual inductance between the fixed and moving coils. These induced currents will flow only when the moving-coil circuit is closed and when the position of the moving system is not at the point of zero mutual inductance. With the moving system displaced 2 degrees of arc (a deflection of 15 cm on the scale) from the point of zero mutual inductance and with rated current at a frequency of 2,000 c/s through the fixed coil, a deflection of 0.50 cm was noted when the moving-coil circuit was closed through an external resistance of 1,000 ohms (without a compensating capacitance). With positions of the moving system at which the wattmeter is generally used (within about 2 cm of the deflection at zero mutual inductance), no noticeable deflection was obtained when the moving-coil circuit was closed through a resistance of 1,000 ohms.

The only appreciable error, entering eq 1 as "$\Delta\alpha$", was found to be that due to eddy currents in the moving system and capacitance currents in the moving coils. The magnitude of this error was measured at various frequencies up to 3,000 c/s with 5 amp through the fixed coils connected in series-parallel and with the moving-coil circuit open, the shield and moving-coil terminal *b* being tied to fixed-coil terminal *b*. The results of these measurements are shown by the curve plotted in figure 8. By means of these results the "$\Delta\alpha$"

errors can be separated from the total ac-dc errors measured in the experiments to be described.

4. ERRORS DEPENDING UPON EI—TEST AT UNITY POWER-FACTOR

(a) METHOD

A simple and convenient way to obtain unity power-factor conditions on the wattmeter is to connect it for use as an ammeter, as shown in figure 7. For these connections, the current in the moving

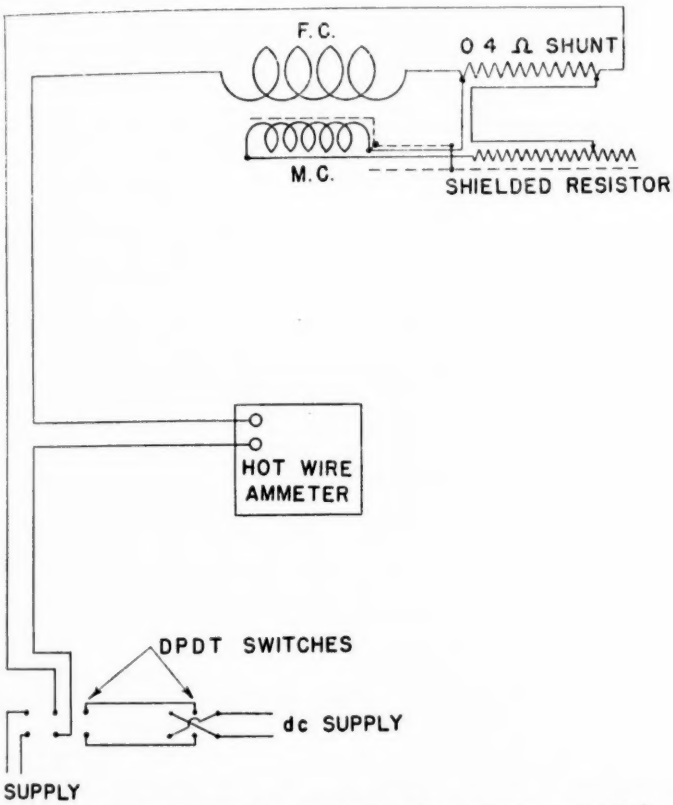


FIGURE 7.—*Electric connections for comparing the wattmeter, connected as an ammeter, with a hot-wire ammeter at unity power-factor.*

coil may be considered to be in phase with the current through the fixed coil. Any slight difference in phase (τ) between these currents will enter into the results as an error equal to 100 (1–cos τ) in percent, and the conditions to be fulfilled in order to make the error negligible are easily attainable. Thus the only ac–dc errors entering this unity power-factor test will be those designated as "Δm" and "$\Delta\alpha$" in eq 1, and these errors will be equivalent to the errors of the wattmeter when it is used to measure power at unity power-factor, provided the moving-coil circuit is properly shielded.

The main reason for connecting the wattmeter as an ammeter to measure its ac–dc errors at unity power-factor [8] was that a 5-amp Hartman & Braun hot-wire ammeter, which was constructed for the accurate measurement of radio-frequency currents, was readily obtainable and convenient to use as a standard. It was assumed that the ac–dc errors of the ammeter are negligible for frequencies up to 3,000 c/s.

(b) PROCEDURE

The procedure consisted in adjusting the alternating- and direct-current supplies independently, so that full-scale deflection of the hot-wire ammeter was obtained for both positions of the ac–dc

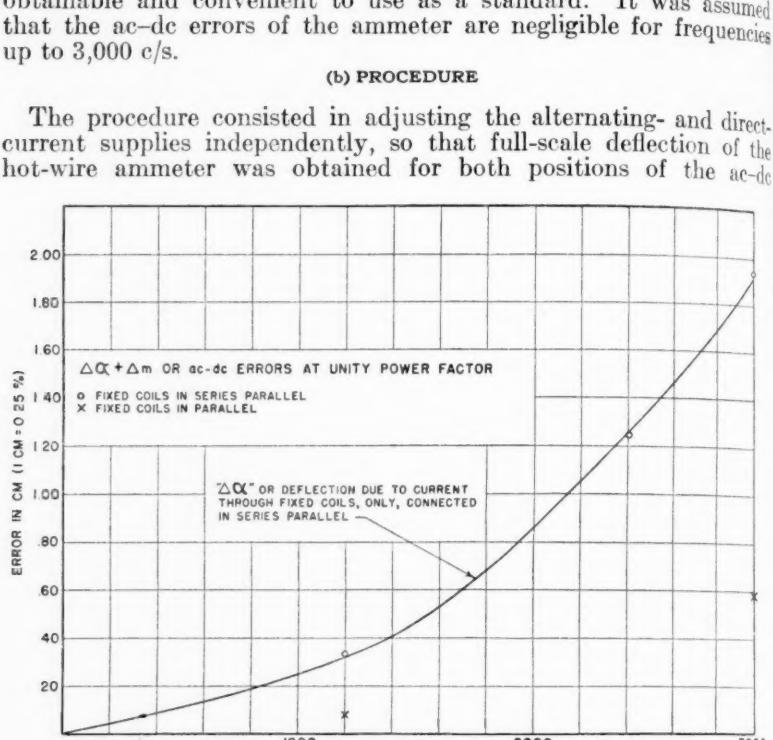


FIGURE 8.—*Wattmeter ac-dc errors at unity power-factor.*

Fixed-coil current equals 5 amp. Moving-coil terminal *b* connected to fixed-coil terminal *b* (see fig. 5). The curve is a plot of "$\Delta\alpha$" errors only. The plotted points include "$\Delta\alpha$" and "Δm" errors.

switch (see fig. 7). The series resistor in the moving-coil circuit of the wattmeter was adjusted to bring the wattmeter deflection to normal full-scale position (this required about 1,300 ohms in the moving-coil circuit), and the current was left on for one-half hour to allow both instruments to come to temperature equilibrium. The test data were taken in the following order: (1) with alternating current of the desired frequency on, the value of current was adjusted to give full-scale deflection on the hot-wire ammeter and the deflection of the wattmeter was read; (2) with direct current on and adjusted to duplicate the setting on the hot-wire ammeter, the deflection of the wattmeter was read; (3) with direct current reversed, another reading of wattmeter deflection was obtained; and (4) with alternating current on, the first step was repeated. The difference between the average a-c (steps 1 and 4 above) and the average d-c

[8] A quadrant electrometer connected to measure power could be used as a standard instrument for this purpose, but a considerable amount of time and patience would be required to set up and calibrate an instrument of this type so that the desired accuracy could be attained.

(steps 2 and 3 above) wattmeter deflections is a measure of the wattmeter ac–dc errors at unity power-factor.

The accuracy of the measurements is limited by the ability of the observer to repeat settings on the hot-wire ammeter. By using an instrument-reading camera focused directly on the pointer and adjusting current until the image of the pointer edge coincides with a fine line on the ground-glass screen of the camera, settings can be repeated to within 0.025 of a scale division. Since each value of ac–dc difference was the average of several sets of data, the accuracy of these average values was considered to be within about 0.01 of a scale division or 0.01 percent (settings were all made at the 100-division point).

(c) RESULTS

For the purpose of comparison the results of these tests have been entered in figure 8. As already noted, the curve in this figure is a plot of the wattmeter deflection "$\triangle\alpha$" against frequency, obtained on a previous test with 5 amp through the wattmeter fixed coils connected in series-parallel and the moving-coil circuit open (this is the deflection due to eddy currents in the moving system and capacitance currents in the moving coils). The plotted points on this figure represent the values of ac–dc errors of the wattmeter at unity power-factor obtained by the tests just described. The agreement of the plotted points with the curve (with the fixed coils connected in parallel only one-half of rated current was used and the ac–dc error is correspondingly less) indicates that for frequencies up to 3,000 c/s the ac–dc errors of the wattmeter at unity power-factor are due only to eddy currents in the moving system and capacitance currents in the moving coils. These errors enter into eq 1 as the term "$\triangle\alpha$". The error designated as "$\triangle m$" in this equation is thus found to be negligible (less than 0.01 percent) for frequencies up to 3,000 c/s.

5. ERRORS DEPENDING UPON PHASE ANGLE θ—TESTS AT ZERO POWER-FACTOR

The ac–dc errors of the wattmeter entering eq 1 as a phase defect "τ_w" will appear only when the wattmeter is used at power factors other than unity, and their effect will be maximum at zero power-factor. Possible sources of phase defect are (1) eddy current or skin effects in the fixed coils, (2) capacitance currents in the fixed coils, and (3) phase defect in the voltage circuit. Since the phase defect introduced by these sources of error increases as the frequency increases, it was decided to determine the phase defect at several frequencies. Tests were made at 60 c/s using a quadrant electrometer and at 500, 1,000, and 2,000 c/s using mica capacitors.

(a) AT 60 CYCLES PER SECOND, USING QUADRANT ELECTROMETER

(1) *Method.*

The source of current and voltage consisted of two alternators driven by a direct-current motor, the shafts of all these machines being coupled together. The motor was supplied from storage batteries, and the speed was adjusted to give a 60-cycle output from each generator. The output voltage of each alternator and the phase angle between their voltages could be varied independently. One alternator was used to supply the voltage circuit of the standard wattmeter, and this

same voltage was connected between the case and the needle of the quadrant electrometer. The other alternator was used to supply the current through the fixed coils of the wattmeter, and by also passing this current through a shunt and then stepping-up the drop across the shunt by means of a voltage transformer whose secondary was connected to the quadrants of the electrometer, a voltage was applied to the quadrants which bore a fixed relation to the current through the wattmeter fixed coils.

The voltage, E, from one of the alternators and the current, I, from the other alternator correspond to a value of power $EI \cos \theta$ which

FIGURE 9.—*Electric connections for comparing the wattmeter with a quadrant electrometer at zero power-factor.*

R=resistance of shunt.
L=inductance of shunt.
r=resistance of shunt potential leads.
R_1=effective resistance of transformer primary winding.
L_1=effective inductance of transformer primary winding.
I_1=transformer primary current.
E_1=transformer primary voltage.
E_a=transformer secondary voltage from a to c.
E_b=transformer secondary voltage from a to b.

can be measured independently by the wattmeter and by the electrometer. The phase angle, θ, between the voltage and current was adjusted until the electrometer indicated zero power. The wattmeter would then be expected to indicate the power corresponding to 90 degrees minus the phase difference between the current through the fixed coils of the wattmeter and the quadrant voltage of the electrometer. A derivation of the value of this phase difference is given in appendix II. Any discrepancy between the actual power indicated by the wattmeter and the power computed from this phase difference is considered to be caused by a phase defect in the wattmeter, and the wattmeter phase-defect was computed on this basis.

(2) *Procedure.*

The wiring diagram in figure 9 was followed in connecting the wattmeter and electrometer for the test at zero power-factor. The voltage, E, was set at 150 (within 0.2 of a volt) by adjusting the field of the

alternator. The current, I, was set at 2.5, 5, or 10 amp (within 0.2 percent), depending upon whether the series, series-parallel, or parallel connection, respectively, of the wattmeter fixed coils was being used. The nominal value of the shunt corresponding to these currents was 0.8, 0.4, or 0.2 ohm, respectively, thus keeping the primary voltage of the transformer 2 volts for all tests. The secondary voltage across each half of the winding was approximately 25 volts. The connection from the transformer secondary to the quadrant of the electrometer was a two-conductor shielded lead, the shield being connected to the transformer shield and the midpoint of the winding at one end and to the electrometer case at the other end. The same leads were used in measuring the ratio and phase angle of the transformer so that any capacitance load imposed by the leads would be the same in both the test and the use of this transformer. The phase angle, Θ, between E and I was adjusted to approximately 90 degrees by rotating the stator of the alternator supplying the current. A fine control of this phase angle was obtained by inserting a variable self-inductor in the current circuit. The 25,000-ohm resistor in series with the lead to the electrometer needle was inserted to protect the needle suspension from possible short circuits between needle and quadrant during preliminary adjustments. For final readings this resistor was shorted out to reduce to a minimum any voltage drop in this lead due to capacitance currents. A switching arrangement was placed in the current and voltage supply such that the alternating current and voltage could be disconnected and a direct current and voltage substituted. The d-c supply was used to calibrate the wattmeter.

The detailed procedure in checking the wattmeter against the electrometer at zero power-factor will now be described in chronological order. The electrometer was set on a stable platform with the needle centrally located with respect to the quadrants, as indicated in figure 9. A light source was located in such a position that the beam reflected from the mirror mounted on the electrometer suspension was focused on a ground-glass scale located about 2 m from the electrometer. The leveling screws of the electrometer were adjusted until the mechanical and electrical zeros of the electrometer coincided (to within 2 mm), that is, with current off and a-c voltage adjusted to 150 v the electrometer reading did not change when switch S_1 was thrown from right to left. The zero readings of both the electrometer and the wattmeter were recorded with no current flowing and $E=150$ v a-c. The current supply was connected and current adjusted to 2.5, 5, or 10 amp a-c depending on the fixed-coil connections of the wattmeter. Frequency was set to 60 c/s and voltage was reset if necessary. The phase angle between E and I was adjusted until the electrometer reading was the same as its zero, and the reading of the wattmeter was recorded. The current supply was disconnected and zero readings of electrometer and wattmeter were recorded. The setting of the electrometer with current on should agree with the average of the two electrometer zero readings (in the few cases where this was not true the readings were discarded). The above procedure was repeated with switch S_2 in the reversed position. The a-c supply was disconnected and the d-c supply was connected, the voltage being adjusted to 150 v. The direct current was adjusted until the wattmeter reading was equal to the average of the two readings obtained

with alternating current. The value of direct current was recorded, direct voltage and current were reversed, and another value of direct current was obtained and recorded. The entire procedure outlined above was repeated with the alternating voltage supply connections reversed. The average of the four values of direct current thus obtained divided by the alternating current gives cos Θ, which should equal $\frac{1}{2}\sin(2\delta+\beta_c+\beta_b)$[9] if there is no phase defect in the wattmeter.

(3) *Results.*

TABLE 2.—*Wattmeter phase defect at 60 c/s*

[This table is not a complete list of all data taken at 60 cycles. The values shown were chosen to indicate the range of variation in τ_w. The average value of all determinations of τ_w at 60 cycles is 0.2 minute]

E_{ac}	I_{ac}	Wattmeter fixed coils	Wattmeter multiplier	Electrometer shunt	90° minus Θ_c	90° minus Θ_m	*$\tau_w = \Theta_c - \Theta_m$
v	*amp*		*Ohms*	*Ohms*	*min*	*min*	*min*
						7.04	0.26
						7.03	.25
						7.08	.30
150	10	Parallel	5,000 s	0.2	6.78	6.99	.21
						6.81	.03
						6.78	.00
						6.77	−.01
						Average	0.13
150	10	do	{5,000 s {1,000 p	.2	6.78	7.19	0.41
						7.06	.28
						Average	0.34
150	10	do	9,000 s	.2	6.78	7.19	0.41
						7.00	.22
						Average	0.32
						7.22	0.44
						7.22	.44
150	5	Series-parallel	5,000 s	.4	7.17	7.14	−.03
						7.07	−.10
						Average	−0.01
						8.70	−0.01
						8.74	−.03
150	2.5	Series	5,000 s	.8	8.71	8.58	−.13
						8.58	−.13
						Average	−0.06

* A positive value of τ_w indicates that the moving coil current leads the supply voltage.

The results of tests at zero power-factor comparing the wattmeter with a quadrant electrometer are tabluated in table 2. The phase defect of the wattmeter is indicated as the difference between two phase angles (1) Θ_c which is 90 degrees minus the computed phase angle between the current through the wattmeter fixed coils and the voltage across the quadrants of the electrometer, and (2) Θ_m which is the power-factor angle measured with the wattmeter while the quadrant electrometer indicated zero watts. The wattmeter phase defect, τ_w, probably consists of two components (1) a phase displacement between the moving-coil current and the voltage applied to the wattmeter voltage circuit, and (2) a phase displacement between the magnetic flux due to the fixed coils and the current supplied to the fixed coils. For convenience in discussing the phase defect, the two components are added and this total phase defect is treated as if it were a phase displacement between the moving-coil current and the wattmeter supply voltage; a positive value of τ_w indicates that the moving-coil current leads the supply voltage. The computed phase angle, θ_c,

[9] For the derivation of this relation see appendix II.

was primarily dependent upon the phase angle of the potential transformer. The phase angle of this transformer had an uncertainty of ± 0.1 minute, probably due to magnetic instability of the core. The experimental error in comparing the wattmeter and the electrometer was ± 0.1 minute. Thus the total uncertainty in τ_w was ± 0.2 minute, which is sufficient to account for the variations of the phase defect of the wattmeter as indicated in the last column of table 2. The conclusion is that the phase defect of the wattmeter at a frequency of 60 c/s is very probably less than 0.4 minute for any fixed-coil connection and for any arrangement of the multiplier circuit as normally used.

(b) AT HIGH FREQUENCIES, USING CAPACITANCE LOAD

(1) *Method and Procedure.*

By passing current through the fixed coils of the wattmeter and a capacitor, connected in series, and applying the voltage drop across the capacitor to the voltage circuit of the wattmeter, the current and voltage of the wattmeter will be very nearly 90 degrees out of phase and the wattmeter deflection should be about zero. The small value of watts indicated by the wattmeter will be due to (1) any phase defect in the capacitor used as a load; (2) the current taken by the voltage circuit of the wattmeter, which necessarily flows through the wattmeter fixed coils; (3) the current taken by the voltmeter used to measure the drop across the capacitor; and (4) any phase defect in the wattmeter. Since the total watts indicated by the wattmeter can be determined and the first three of the above factors making up the total watts can be computed or measured, the fourth factor (wattmeter phase defect) can be deduced.

The capacitance used as a load on the wattmeter must have a value such that with the normal wattmeter voltage across it (about 150 v), the current taken will be equal to the rated current of the wattmeter fixed coils (2.5, 5, or 10 amp). It would be almost impossible to build up enough capitance by using air capacitors. Paper capacitors have losses too large and too unstable. Mica capacitors were considered feasible for this work, and the largest capacitance which could be built up from all of the mica capacitors readily available was about 10 μf. With these capacitors it was possible to test the wattmeter at frequencies of 500 to 2,000 c/s. It was decided to measure the phase defect of the wattmeter at 500, 1,000, and 2,000 c/s and then if possible to extrapolate the results back to lower frequencies.

The wiring diagram for the equipment used in this test is shown in figure 10. A Kelvin voltmeter of the multicellular electrostatic type was used to measure the voltage across the wattmeter voltage circuit, because the deflection of this type of voltmeter is independent of frequency over a wide range. A resistance voltage divider was used in conjunction with this voltmeter to extend its range, since the maximum voltage which could be read on the voltmeter alone was 120 v. An attempt was made to extend the range of this voltmeter by putting an air capacitor in series with it, but this plan had to be abandoned because of an error introduced by dielectric losses in the voltmeter.

With switch S_2 (see fig. 10) thrown to the right-hand position the wattmeter measures the power loss in capacitor C, the power consumed in r_m and r_v, and an additional quantity $\omega CE^2 \sin \tau_w$, where τ_w is

the phase defect of the wattmeter. With switch S_2 thrown to the left-hand position the wattmeter measures the power consumed in r_m, r_v, and R. Under these conditions the current through the wattmeter fixed coils is small in value compared to the large capacitance current taken by C and is in phase with the voltage, E, across the wattmeter voltage circuit, so that the effect of the wattmeter phase defect is negligible. The procedure followed in measuring the wattmeter phase defect, τ_w, was first to set the supply frequency and voltage with switch S_2 in the right-hand position and read the wattmeter deflection, then to duplicate the setting of supply frequency

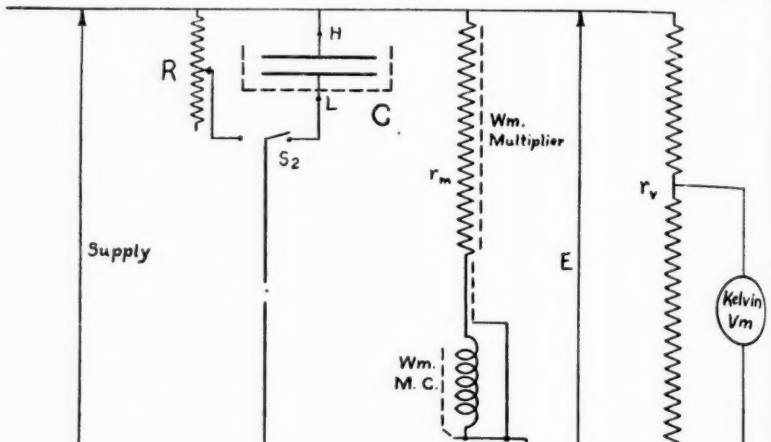


FIGURE 10.—*Electric connections for measuring wattmeter phase defect at high frequencies using a capacitance load.*

C=mica capacitor.
R=adjustable resistor.
r_m=resistance of wattmeter voltage circuit.
r_v=resistance of voltage divider for electrostatic voltmeter.
E=voltage applied to wattmeter voltage circuit.

and voltage with S_2 in the left-hand position and adjust the resistor, R, until the wattmeter deflection was the same as just read. The wattmeter phase defect can then be deduced from the value of the resistor, R, capacitor, C, and phase defect, τ_c, of capacitor C.

(2) *Derivation of Equation.*

By referring to the wiring diagram in figure 10 and using the notation indicated on the diagram, two equations for the quantity measured by the wattmeter can be written. When the capacitor, C, is used as a load on the wattmeter (switch S_2 to the right) the quantity is

$$P_c=\omega CE^2 \sin (\tau_c+\tau_w)+\frac{E^2}{r_m}+\frac{E^2}{r_v}.$$

When the resistor, R, is used as a load on the wattmeter (switch S_2 to the left), this quantity is

$$P_R=\frac{E^2}{r_n}+\frac{E^2}{r_v}+\frac{E^2}{R}.$$

During the tests, the voltage, E, and the deflection of the wattmeter were held constant for the two loads on the wattmeter. Thus $P_c = P_R$, and the two equations give

$$\omega C \sin(\tau_c + \tau_w) = \frac{1}{R};$$

and since τ_c and τ_w are small angles,

$$\sin \tau_w = \frac{1}{R\omega C} - \sin \tau_c. \tag{2}$$

(3) *Results.*

The results of these tests are shown in figure 11 as a plot of wattmeter phase defect against frequency. The error ($\Delta\alpha$) due to induced currents in the moving system and capacitance currents in the moving coils is present in the results shown, but its magnitude (a maximum of 2 minutes at 2,000 c/s) was not sufficient to be taken into account. The possible sources of this phase defect are (1) eddy current or skin effects in the fixed coils, (2) phase defect in the voltage circuit, and (3) capacitance currents between turns of the fixed coils and from fixed coils to shield. Possible source of error (3) would cause a phase defect proportional to the square of the frequency, but the results show the phase defect to be directly proportional to frequency; also, when performing the tests, a $0.005-\mu f$ capacitor connected across the fixed coils was found to have no noticeable effect on the phase defect. Therefore, it may be concluded that source of error (3) is negligible for frequencies up to 2,000 c/s. Sources of error (1) and (2) would cause a phase defect directly proportional to frequency. Since the observed phase defect was found to vary in this manner (up to 2,000 c/s), it may be concluded that it is the result of one or both of these two effects.

A computation of the part of this phase defect caused by source (2), based on the estimated values of capacitance between parts of the voltage circuit, indicated that part of the wattmeter phase defect can be accounted for by the capacitance currents in the series resistor. The remainder of the wattmeter phase defect must be due to "skin effects" in the fixed coils. The relative magnitude of these two components of the total wattmeter phase defect cannot be definitely stated.

Since the results shown in figure 11 indicate that the wattmeter phase defect is directly proportional to frequency between 500 and 2,000 c/s, it is fairly safe to extend this curve to 60 c/s and obtain an extrapolated value of phase defect of 0.38 minute. This extrapolated value checks the actual value (0.2 minute) [10] obtained at 60 c/s, using the quadrant electrometer, within the limits of accuracy (± 0.2 minute) of the measured value.

IV. SUMMARY

The electrodynamic instrument described in this paper can be used as a standard wattmeter or ammeter and as a standard ac–dc transfer instrument in testing wattmeters or ammeters. The current range is from 0.25 to 10 amp. The voltage range is from 25 to 300 v. The

[10] This value is an average of all the data taken at 60 c/s.

results obtained from this instrument are accurate within 0.01 percent when it is used at power frequencies. The only correction which must be applied to obtain this accuracy is the one due to the phase defect

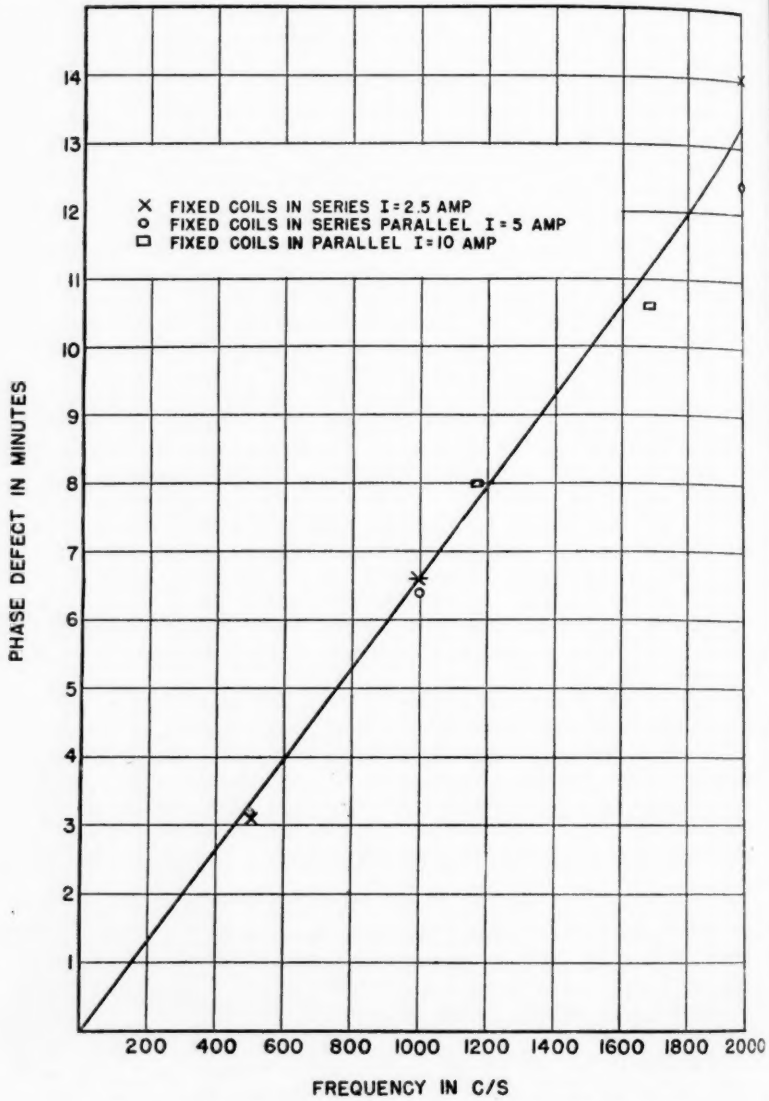


FIGURE 11.—*Plot of wattmeter phase defect against frequency.*

Results obtained from tests using a capacitance load.

(0.38 minute at 60 c/s). This correction will be negligible for power factors greater than 0.7. The instrument can also be used at frequencies up to 2,000 c/s, provided the necessary corrections as described in this paper are applied.

Almost all the construction of this transfer instrument was done by E. A. Tibbals, one of the Bureau's mechanicians, who is responsible for many valuable suggestions relating to the design of important details of the instrument.

V. APPENDIX I

Computation of the Effect of Variation in Wattmeter Sensitivity

The wattmeter deflection in terms of S, wattmeter sensitivity (equal to G/U as defined on page 559); i, moving-coil current in milliamperes; and I, fixed-coil current in amperes is

$$\alpha = Si\frac{I}{I\,(\text{rated})}.$$

The power being measured is proportional to Ii, and I (rated) is constant for a given connection of the fixed coils. Thus the deflection may be expressed as

$$\alpha = KSW,$$

where K is a constant and W is the power being measured. If α_a, S_a, and W_a denote values with alternating current and voltage; α_d, S_d, W_d denote values with direct current and voltage; α_r, S_r, W_r denote values with direct current and voltage in the reverse direction

$$\alpha_a = KS_aW_a, \text{ or } W_a = \frac{\alpha_a}{KS_a};$$

$$\alpha_d = KS_dW_d, \text{ or } W_d = \frac{\alpha_d}{KS_d};$$

$$\alpha_r = KS_rW_r, \text{ or } W_r = \frac{\alpha_r}{KS_r}.$$

The relation to be obtained is the ratio of W_a to the average d-c power in terms of the α's and S's.

$$\frac{2W_a}{W_d+W_r} = 1+\frac{W_a-\frac{1}{2}(W_d+W_r)}{\frac{1}{2}(W_d+W_r)} = 1+\delta.$$

Substituting values of α and S, δ becomes

$$\delta = \frac{\frac{\alpha_a}{KS_a}-\frac{1}{2K}\left(\frac{\alpha_d}{S_d}+\frac{\alpha_r}{S_r}\right)}{\frac{1}{2K}\left(\frac{\alpha_d}{S_d}+\frac{\alpha_r}{S_r}\right)}.$$

Since S_d and S_r differ but slightly from S_a, by putting $S_d = S_a+s_d$ and $S_r = S_a+s_r$ the above equation simplifies to

$$\delta = \frac{\alpha_a-\frac{\alpha_d+\alpha_r}{2}}{\frac{\alpha_d+\alpha_r}{2}}+\tfrac{1}{2}\left(\frac{s_r+s_d}{S_a}\right).$$

One hundred times the first term on the right side of the above equation gives the percentage excess of a-c power over average d-c power as normally computed assuming constant sensitivity. One hundred times the second term gives the correction in percentage to be applied when the sensitivity for α_d and α_r are different from the sensitivity for α_a. Values of S_a, s_r, and s_d are obtained from the curves of sensitivity against deflection in figure 6.

VI. APPENDIX II

Phase Difference Between the Fixed-Coil Current and the Quadrant Voltage on the Electrometer and the Relation of This Phase Difference to Θ, the Phase Angle Between E and I

The diagram in figure 9 shows the connections of the wattmeter and the electrometer for measuring the power $EI\cos\Theta$. The first step is to derive the relation between I and E_c or E_b in terms of the known constants of the apparatus. By inspection of the diagram and using the notation given under it, the following equation can be written

$$I_t(R_t+j\omega L_t)=-I_t 2r+(I-I_t)(R+j\omega L). \tag{3}$$

The currents in this equation are all complex quantities, but I may be assumed to have no imaginary component. By equating the real and imaginary components of eq 3 and solving for the two components of I_t, these may be substituted in

$$E_1=I_t(R_t+j\omega L_t)$$

to obtain:

$$E_1=I\left\{\frac{(R_tR-\omega^2L_tL)(R_t+R+2r)+(\omega LR_t+\omega L_tR)(\omega L_t+\omega L)}{(R_t+R+2r)^2+(\omega L+\omega L_t)^2}\right.$$
$$\left.+j\,\frac{[(\omega L_tR+\omega LR_t)(R_t+R+2r)+(\omega^2L_tL-R_tR)(\omega L_t+\omega L)]}{(R_t+R+2r)^2+(\omega L+\omega L_t)^2}\right\}.$$

For the present work the approximate values of the constants in the above equation are $R=0.4$ ohm, $R_t\geqq 400$ ohms, $r=0.03$ ohm, $L=30\times10^{-9}$ h, $\omega L_t\geqq 600$ ohms.

Thus with sufficient accuracy the equation may be reduced to

$$E_1=IR\left[1-(2r+R)\frac{R_t}{R_t^2+\omega^2L_t^2}+j\frac{\omega L}{R}+j(R+2r)\frac{\omega L_t}{R_t^2+\omega^2L_t^2}\right];$$

and putting

$$g=(2r+R)\frac{R_t}{R_t+\omega^2L_t^2}$$

and

$$\delta=\sin^{-1}\left[\frac{\omega L}{R}+(R+2r)\frac{\omega L_t}{R_t+\omega^2L_t^2}\right],$$

$$E_1=IR(1-g+j\sin\delta). \tag{4}$$

If the ratios and phase angles for the transformer are n_c, β_c and n_b, β_b for the ac and ab coils respectively,

$$E_c=n_cE_1(1+j\sin\beta_c)$$

and

$$E_b=n_bE_1(1+j\sin\beta_b).$$

Substituting the value of E_1 given in eq 4 and neglecting the products of the sines of the small angles δ, β_c, and β_b,

$$E_c=n_cIR[1-g+j(\sin\delta+\sin\beta_c)] \tag{5}$$

and

$$E_b=n_bIR[1-g+j(\sin\delta+\sin\beta_b)]. \tag{6}$$

For the connections of the quadrant electrometer shown in figure 9, if V_n is the voltage from the case to needle, V_c from case to quadrant c, and V_b from case to quadrant b, the general equation for the torque is

$$T=\lambda V_n^2+\rho_cV_c^2+\rho_bV_b^2+\gamma_cV_nV_c+\gamma_bV_nV_b+\eta V_cV_b+\nu_nV_n+\nu_cV_c+\nu_bV_b+\nu_0,$$

where λ, ρ_c, ρ_b, γ_c, γ_b, η, ν_n, ν_c, ν_b, and ν_0 are constants of the electrometer. Take the mechanical zero to be the reading when c, b, and n are all tied to the case, that is, with current circuit open and S_1 to the right. This makes $\nu_0=0$. For a-c work ν_n, ν_c, and ν_b can also be ignored, because the mean values of V_n, V_c, and V_b over any number of complete cycles is zero. The electrical zero is adjusted by tilting or rotating the needle until no deflection occurs when S_1 is thrown to the left. This makes $\lambda=0$. With both current and voltage on, the torque then becomes

$$T_1=\rho_c V_c^2+\rho_b V_b^2+\gamma_c V_n V_c+\gamma_b V_n V_b+\eta V_c V_b.$$

The phase angle, Θ, between the current and the voltage is adjusted until the average torque becomes zero, that is, until the electrometer reading is the same as its electrical zero, then

$$0=\rho_c n_c^2 R^2 I^2+\rho_b n_b^2 R^2 I^2+\gamma_c n_c EIR[\cos(\Theta-\delta-\beta_c)]$$
$$-\gamma_b n_b EIR[\cos(\Theta-\delta-\beta_b)]-\eta n_c n_b R^2 I^2 \qquad (7)$$

With switch S_2 reversed, that is E_c and E_b reversed, Θ is again adjusted until the average torque becomes zero. Then

$$0=\rho_c n_c^2 R^2 I^2+\rho_b n_b^2 R^2 I^2-\gamma_c n_c EIR[\cos(\Theta'-\delta-\beta_c)]$$
$$+\gamma_b n_b EIR[\cos(\Theta'-\delta-\beta_b)-\eta n_c n_b R^2 I^2. \qquad (8)$$

Subtract eq 8 from eq 7

$$0=\gamma_c n_c EIR[\cos(\Theta-\delta-\beta_c)+\cos(\Theta'-\delta-\beta_c)]$$
$$-\gamma_b n_b EIR[\cos(\Theta-\delta-\beta_b)+\cos(\Theta'-\delta-\beta_b)].$$

Expanding the cosines in this equation and neglecting the departure from unity of $\cos(\delta+\beta_c)$, $\cos(\delta+\beta_b)$, $\sin\Theta$, and $\sin\Theta'$ since $\delta+\beta_c$ or $\delta+\beta_b$ <10 minutes and Θ or Θ' is within 10 minutes of $\pi/2$

$$\gamma_c n_c[\cos\Theta+\sin(\delta+\beta_c)+\cos\Theta'+\sin(\delta+\beta_c)]$$
$$=\gamma_b n_b[\cos\Theta+\sin(\delta+\beta_b)+\cos\Theta'+\sin(\delta+\beta_b)]$$

Since γ_c very nearly equals $-\gamma_b$ and n_c nearly equals n_b, $-\gamma_c n_c(1+h)$ may be substituted for $\gamma_b n_b$; then

$$\cos\Theta+\cos\Theta(1+h)+\cos\Theta'+\cos\Theta'(1+h)=-2\sin(\delta+\beta_c)-2[\sin(\delta+\beta_b)](1+h),$$

and this reduces to

$$\cos\Theta+\cos\Theta'=-[\sin(\delta+\beta_c)]\left(1-\frac{1}{2}h\right)-[\sin(\delta+\beta_b)]\left(1+\frac{1}{2}h\right),$$

Since β_c nearly equals β_b the h terms cancel, and dividing by 2 to get the average $\cos\Theta$

$$\frac{\cos\Theta+\cos\Theta'}{2}=-\frac{1}{2}\sin(2\delta+\beta_c+\beta_b). \qquad (9)$$

This equation yields the average value of the cosine of the angle between current I and voltage E, for the two positions of switch S_2, in terms of the constants of the apparatus in the electrometer circuit. The cosine of this angle can also be obtained from the expression

$$W=EI\cos\Theta,$$

where W is the average power indicated by the wattmeter for the two positions of switch S_2. Any difference between the two values of $\cos\Theta$ thus obtained is considered to be caused by the wattmeter phase defect, τ_w.

WASHINGTON, July 25, 1940.

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A MULTIPURPOSE PHOTOELECTRIC REFLECTOMETER

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ABSTRACT

The multipurpose reflectometer was developed primarily to measure apparent reflectance, specular gloss, and trichromatic coefficients. These measurements are useful in the ceramic, paint, textile, paper, and chemical industries to indicate lightness, gloss, and color of finished articles. In the reflectometer, two light beams from a single source are directed along separate paths to two barrier-layer photocells. Various types of these photocells were studied to find which could be used most advantageously. The reflectometer employs a substitution null method and requires a galvanometer to indicate equality of the currents generated by the two photocells. For each sample tested, there is a photometric adjustment to restore equality of the currents. The amounts of photometric adjustment are measured on the direct-reading scales, one of which is used for apparent reflectance and the other for specular gloss. Because of its high precision, the instrument is well suited for measuring small differences in apparent reflectance, gloss, or color of nearly identical samples. However, for greatest accuracy, it is necessary to correct the scale readings by calibration.

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I. INTRODUCTION

The multipurpose photoelectric reflectometer is the result of an attempt to combine in one instrument means for measuring (1) 45°,0° luminous apparent reflectance relative to a standard, (2) 45°,0° apparent reflectance relative to a standard through filters for either tristimulus colorimetry or abridged spectrophotometry, (3) four of the six listed types of gloss [27],[1] and (4) the transmission of clear liquids and optical filters having plane parallel faces.

The development of the multipurpose reflectometer, its construction, its calibration, and its applications are described in the present paper. Further information on the instrument and its use may be found in a paper by Scofield [53] and in a report by the Institute of Paper Chemistry [33].

The multipurpose reflectometer is one of a series of null-method instruments developed by the author to measure 45°,0° apparent reflectance relative to a standard. The two earlier reflectometers are briefly described herein. The first (fig. 5) was a 0°,45° visual reflectometer using a pattern mirror [25]. The aim in building this model was to make a null-method instrument that was simple, could be constructed from inexpensive and readily obtainable materials, and would take relatively large areas of test surfaces. The Committee on Standardization of Tests of the Porcelain Enamel Institute studied this instrument for possible use to measure the apparent reflectances of porcelain-enamel surfaces. They inquired if an instrument of the same character could be photoelectric rather than visual. In answer to this inquiry, two Photox barrier-layer photocells and a galvanometer were substituted for the eye and pattern mirror of the visual instrument, the result being the Photox 0°,45° reflectometer (fig. 6) [6, 26].

Following the successful development of a reflectance test [49], in which this Photox reflectometer was used, the same Committee of the Porcelain Enamel Institute turned to the development of tests of porcelain enamels for resistance to acids [50] and to surface abrasion [51]. For these tests, an instrument for measuring specular gloss was required. It was suggested that an instrument for measuring both specular gloss and 45°,0° apparent reflectance would be doubly useful. The first objective of the present project was to design an instrument meeting this dual need.

To develop apparatus suitable for certain colorimetric measurements was the second objective. In a paper on photoelectric colorimeters, Gibson [18] pointed out that a number of instruments have been developed during the past few years supposedly to measure "color" by means of an illuminant, three spectral filters—usually red, green, and blue—and some type of barrier-layer photoelectric cell. He showed how filters spectrally suitable for photoelectric tristimulus colorimetry ought to be chosen with respect to photocell and illuminant. It is possible to show that, in addition to filters which are properly chosen with respect to photocell and illuminant, a measuring technique capable of unusually high photometric precision is necessary for photoelectric tristimulus colorimetry if the resulting measurements are to identify the smallest color differences of interest. The present paper considers the problem of obtaining high precision, but the selection of proper filters and use of the data obtained therewith are left for subsequent consideration [29].

[1] Figures in brackets indicate the literature references at the end of this paper.

A third objective was to improve the methods of gloss measurement. In an earlier paper [27], six separate types of gloss were listed, four of which should be subject to photometric measurement. Measurement of specular gloss was required by the Porcelain Enamel Institute; two of the remaining three types, contrast gloss and sheen, have been measured with the multipurpose reflectometer; measurement of absence-of-bloom gloss, the fourth type, has been planned, but not actually tried.

Although not projected in the original plans, a device suitable for measuring the transmission of clear solids and liquids was obtained by making a slight adjustment of the attachment for 75°,—75° specular gloss (sheen). The spectral filters used for reflection measurements are available for transmission measurements also and make possible tristimulus colorimetry and abridged spectrophotometry of transmitting specimens. Inasmuch as many of the so-called colorimetric methods of chemical analysis are simply methods of abridged spectrophotometry, the multipurpose instrument may be used as an analytical instrument for the chemical laboratory.

II. TERMINOLOGY

In this paper, psychophysical terms are used to denote the quantities measured, even though they are properly radiometric because photocells rather than human eyes are the responding mechanisms. Instead of light, radiant energy should properly be spoken of; instead of illumination, irradiation; and so forth [35]. However, the use in the present apparatus of source-filter-photocell combinations which measure properties similar to those detected by the human eye was taken as sufficient justification for using the better known psychophysical terms in the present paper.

The term "apparent reflectance" [43] used in this paper, having come into general use only recently [1, 27, 30, 37, 45], deserves a word of explanation. Surfaces, when illuminated, usually do not appear uniformly bright from all directions. The *reflectance* of a surface is, by definition, the ratio of the total quantity of reflected light to the total quantity of incident light regardless of directions. Apparent reflectance, on the other hand, always refers to some specified condition of view. To connect the terms "reflectance" and "apparent reflectance," the concept of the ideal perfectly diffusing surface which reflects according to Lambert's law and appears uniformly bright from all directions is used. The *apparent reflectance* of a surface for the given directions[2] of illumination and viewing is defined as the reflectance which a perfectly diffusing surface would need to possess in order to appear equally bright under the same conditions. The symbol for apparent reflectance is $A_{\theta i,\theta v}$, where Θi and Θv are respectively the angles of illuminating and viewing measured from the normal. In the present paper, *luminous* apparent reflectance is inferred when apparent reflectance is spoken of; also, it is assumed that when both illuminating and viewing beams are unidirectional, they lie in a single plane perpendicular to the surface.

Measurements of apparent reflectance are both useful and practical. A person viewing a surface never observes it from all directions simultaneously, but from some single direction. An apparent-reflectance

[2] Multidirectional as well as single directions of illuminating and viewing may be involved in apparent reflectance designations. Thus on page 604, below, reference is made to $A_{\text{diffuse, }0°}$ as well as to $A_{45°,0°}$.

value will designate the reflectance which this surface appears to have when viewed from this single direction. Moreover, apparent-reflectance measurements for many conditions, among them 45° illumination and 0° viewing, give results for most opaque surfaces so similar to the true reflectances [43] that they are often used instead. Apparent-reflectance measurements, it should be noted, are more easily made than reflectance measurements, which, for each surface measured, require either many determinations with a goniophotometer and integration to give the final result, or the use of an absolute reflectometer.

Illumination at 45° and normal viewing have been internationally adopted as standard conditions for colorimetry of opaque surfaces [54] because they represent a satisfactory average of the directional conditions under which surface colors are observed in everyday life. Values obtained for the reciprocal conditions, normal illumination and 45° viewing, are by the reciprocity law [43] equivalent to 45°,0° values for the same surfaces.

In the direction of mirror reflection and adjacent directions, the apparent reflectances of surfaces are usually much higher than in other directions. The shininess of surfaces is evidence of this high apparent reflectance.

III. PHOTOCELLS AND ELECTRIC CIRCUIT

Barrier-layer photocells possess three advantages for colorimetric and photometric apparatus: (1) The cells are simple and rugged in construction; (2) they generate an emf directly from the light flux incident upon them, so that no externally applied potentials are required for their operation; and (3) they respond more strongly to energy of the visible spectrum than to other energy. On the other hand, there are a number of recognized disadvantages of the cells. Possible methods of compensating for or of overcoming these disadvantages were made the subject of a study prior to designing the reflectometer. A number of cells of different types were investigated under the operating conditions expected in the proposed instrument.

The circuit which seems to come nearest to eliminating the undesirable types of barrier-layer photocell behavior is a null circuit in which two cells are connected with opposite polarities to the terminals of a galvanometer. The resulting current-balancing circuit has been widely used [3] and was employed by the author in the Photox reflectometer (see fig. 6, below) because of the recommendation given by Wood [59]. When the current-balancing circuit is used, the light source of the instrument may be operated directly from electrical supply lines, rather than from a special constant-voltage supply. Because of its success in the Photox reflectometer, this null circuit was adopted for the multipurpose instrument.

The examination of barrier-layer photocells for possible use in the multipurpose reflectometer was conducted under the operating conditions expected in the new instrument. Photocell current was studied in its relation to the wavelength of illumination, the amount of illumination, the duration of exposure, and the temperature. To study the effects of the first two factors, manufacturers' data describing the cells were examined. To study the effects of duration of exposure

[3] Fourteen instances of the use of this circuit, including the Photox reflectometer, are mentioned by Brice [5].

and of temperature, tests were made on cells of four types. Most of the data on photocells given herein were collected in 1936 and 1937, at the time the multipurpose reflectometer was started. They may not be characteristic of similarly named photocells manufactured at the present time.

The spectral sensitivity of a cell must be known before it can be used with confidence in an instrument to measure either luminous properties or trichromatic coefficients. Figure 1 gives the spectral responses (reported by manufacturers) for three barrier-layer photocells, each plotted approximately to unit maximum, and also the ICI standard luminosity (visibility) curve [19, 36] for comparison. It is

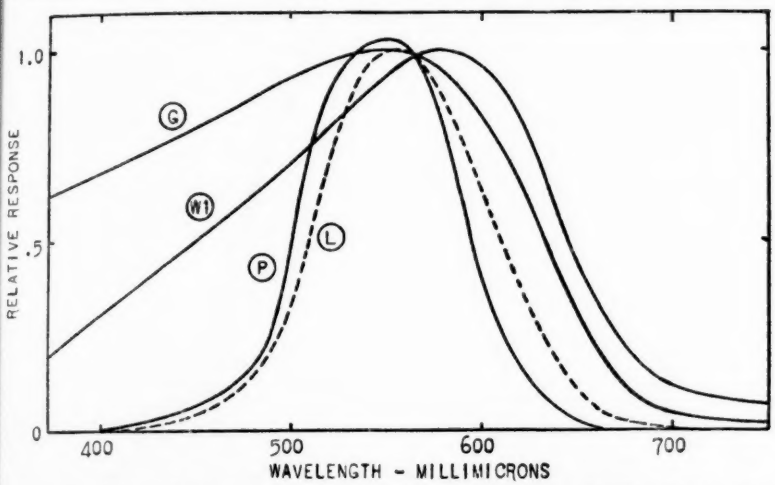

FIGURE 1.—*Spectral-response curves, reported by manufacturers, for three barrier-layer photocells together with ICI luminosity (visibility) function, L.*
G, GE light-sensitive cell; *W1*, Weston Photronic cell, type 1; *P*, Photox cell.

believed that most barrier-layer photocells are characterized by spectral-response curves similar to some one of those shown.

Thus the spectral-response curve published for the Lange photoelectric cell [41, 48] is similar to the Photronic type 1 curve [57], whereas the published curves for the Photronic type 2 cell [57] and the Electrocell [4] are similar to that of the GE cell [16, 17].

In considering uses of the multipurpose reflectometer, the present paper reports, as was noted above, only the measurement of luminous properties, such as luminous apparent reflectance, luminous transmission, gloss, and opacity. Spectral characteristics of the two combinations, which have been used in the multipurpose reflectometer to measure luminous properties, are plotted in figure 2 together with the distribution resulting from multiplying the ICI luminosity function (representing an average normal observer) by ICI illuminant *C*. ICI illuminant *C* is an illuminant [36, 54] of known spectral distribution which is representative of average daylight. The two combinations are (1) the spectral response of a GE barrier-layer photocell to light from an incandescent source at 3,100°K passed through a specified green filter and (2) the spectral response of an average Photox cell

[4] Given in a paper by Parker before the September 1940 meeting of the Illuminating Engineering Society.

to an incandescent source operating at 2,840°K. The GE cell is used in multipurpose reflectometers intended for measuring both luminous and chromatic properties. Without a filter, the spectral response of the Photox cell to a source at 2,840°K is roughly similar to that of the average human observer as represented by the standard luminosity function. Although the Photox cell without filter does not provide as satisfactory duplication of the luminosity function as does the GE cell with the green filter, it has been used with success both in the

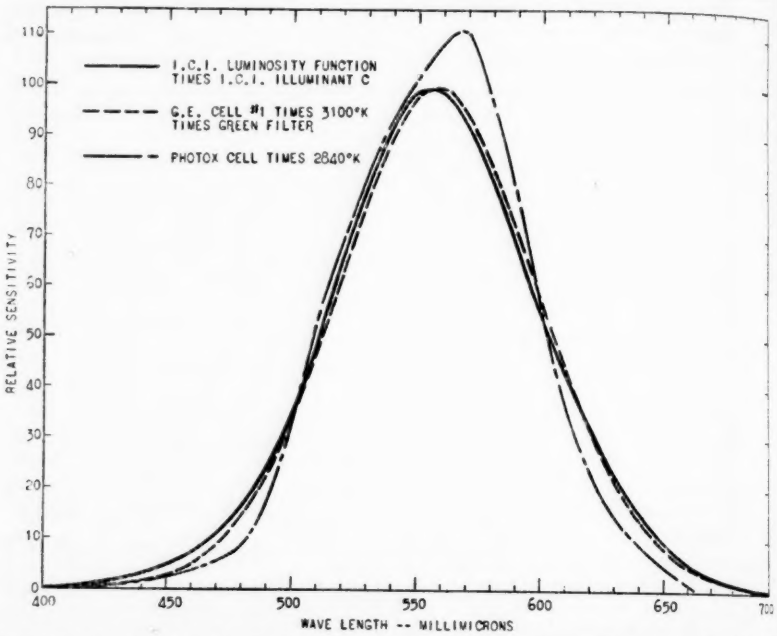

FIGURE 2.—*ICI luminosity function times ICI illuminant C compared with (1) spectral response of GE cell times spectral transmission of green filter times spectral energy of 3,100°K, and (2) spectral response of Photox cell times spectral energy of 2,840°K.*

The green filter is Corning 330 Signal Yellow, 2.7 mm of melt of 11-9-31, plus Corning 428 Light Shade Blue Green, 3.5 mm of melt of 11-2-37 [7]. (The areas under each of the three curves are equal.)

Photox reflectometer and in those multipurpose reflectometers intended only for the measurement of luminous properties.

A number of combinations of filter and barrier-layer photocell have been designed by others to measure luminous properties. The Weston Photronic type 1 cell with Viscor filter described by Gage [14, 57], the GE cell with green filter described by Barnes [3], the G–M Visitron cell with "visual correction filter" [13], have all been designed to evaluate the lightness and brightness of samples under whatever illuminant is actually present. On the other hand, the GE cell with filter specified in figure 2 and the Photox cell with no filter are each offered for use with a designated incandescent illuminant to evaluate samples for lightness as they would appear to the human eye under ICI illuminant *C*. In other words, provision is made in the multipurpose reflectometer for the simultaneous conversion from

photocell response to luminosity-function response and for the change of illuminant from actual incandescent to artificial daylight. The effect of daylight illumination is thus secured without the use of a daylight filter.

In addition to their use for reporting spectral sensitivities, manufacturers' data were consulted to find the currents produced by the different photocells under a given illumination. In table 1 the photocell currents for 1 foot-candle of incandescent-lamp illumination and zero external potential are tabulated together with the dimensions of the respective cells and the current per unit area of sensitive surface. The information in table 1, showing that the well-known Weston Photronic type 1 cell gives relatively low current, and in figure 1, showing that the same cell possesses relatively low sensitivity to blue light (compared with the GE cell), eliminated this cell from consideration for possible use in the multipurpose reflectometer. The response of the Photox cell is also low, but the amount of light incident upon it need not be diminished by passage through a filter in order to measure luminous properties.

TABLE 1.—*Currents generated by barrier-layer photocells in current-balancing circuits (potential across cell terminals at zero)*

Cell name and literature	Active area		Current in microamperes per foot-candle [a]	
	Dimensions (diam.)	Area	Total	Per cm²
	cm	*cm²*		
Weston Photronic, model 594 (original, or type 1) [57]	3.8	11.4	1.43	0.12₅
Westinghouse Photox, style 836107 [56]	5.1	20.3	2.9	.14
Weston Photronic, model 594, type 2 [57]	3.8	11.4	4.2	.37
Lange photoelectric cell No. 1202, type S50 [41, 48]	3.8	11.4	4.5	.39
Electrocell No. 781 [42]	3.8	11.4	5.6	.49
GE round "Hewlett" cell,[b] [16] (removed from market, 12-37)	4.6	16.7	7.8	.47
GE light-sensitive cell [17]	3.8×1.9	7.1	3.4	.48

[a] Although not so stated in every source, it is believed that these figures refer to incandescent-lamp illumination.

[b] The round GE cell was withdrawn from the market at the end of 1937, and in its place a smaller "GE light-sensitive cell" having a rectangular face was offered. Use of the smaller cell in a multipurpose reflectometer requires a more sensitive current indicator than was needed with the large cell.

To measure the effects of temperature and duration of exposure, cells of four types were studied by the author. At the time of these studies, the GE cell was available only in the round model; the rectangular cell having similar characteristics and in wide use today had not appeared. The changes of current from five round GE cells, three Westinghouse Photox cells, three Weston Photronic type 2 cells, and three Electrocells were measured while the cells were under constant illumination of approximately 2 foot-candles. The circuit used was designed by Barbrow [2] to measure the current of a barrier-layer photocell in a current-balancing circuit. The results are shown graphically in figure 3. As a measure of fatigue, each cell was exposed to an incandescent lamp giving it an illumination of 2 foot-candles, and the current during a period of 3 minutes from initial exposure was plotted as a fraction of the current 15 seconds from the start. In demonstrating the influence of temperature, the current generated by each photocell was plotted as a fraction of the current at about 40° C.

In figure 4 are curves giving the currents from one photocell of each type at three levels of illumination. For this figure, 25° C instead of 40° C was chosen as the reference temperature.

Figures 3 and 4 show that use of the current-balancing circuit is no guarantee that the behavior of barrier-layer photocells will be

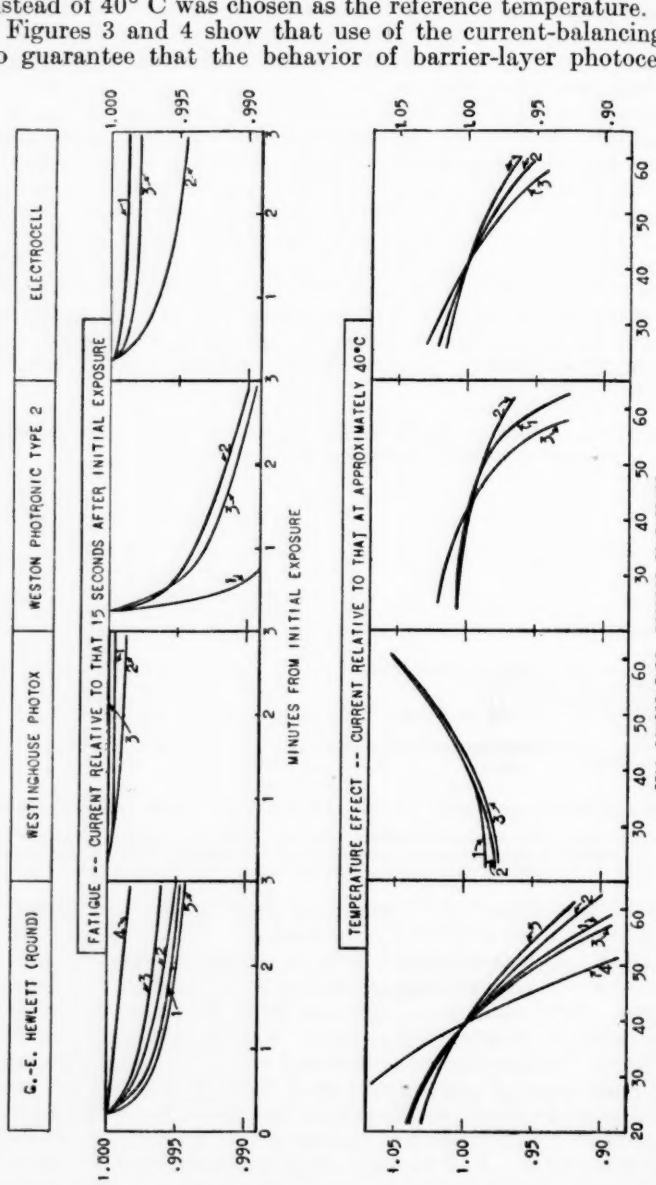
G.-E. HENLETT (ROUND)
WESTINGHOUSE PHOTOX
WESTON PHOTRONIC TYPE 2
ELECTROCELL
FATIGUE -- CURRENT RELATIVE TO THAT 15 SECONDS AFTER INITIAL EXPOSURE
MINUTES FROM INITIAL EXPOSURE
TEMPERATURE EFFECT -- CURRENT RELATIVE TO THAT AT APPROXIMATELY 40°C
CELL TEMPERATURE, DEGREES CENTIGRADE

FIGURE 3.—*Currents of different barrier-layer photocells as a function of (1) duration of exposure and (2) temperature.*

Cell terminals at zero potential, incandescent source with no filters, cell illumination of 2 foot-candles. Numbers identify curves of individual cells.

automatically duplicated from cell to cell, even when the two cells are of the same type. Two photocells to be used together in a multipurpose or Photox reflectometer must have similar fatigue characteristics and similar spectral responses. If, moreover, the instrument in which they are used is to operate from ordinary electrical supply, the

two cells must change response identically whenever the source changes in intensity because of a change in line voltage. If the two cells in an instrument do not meet these requirements, the device will operate in an unsteady manner and fail to give reproducible readings (see the study of errors, below).

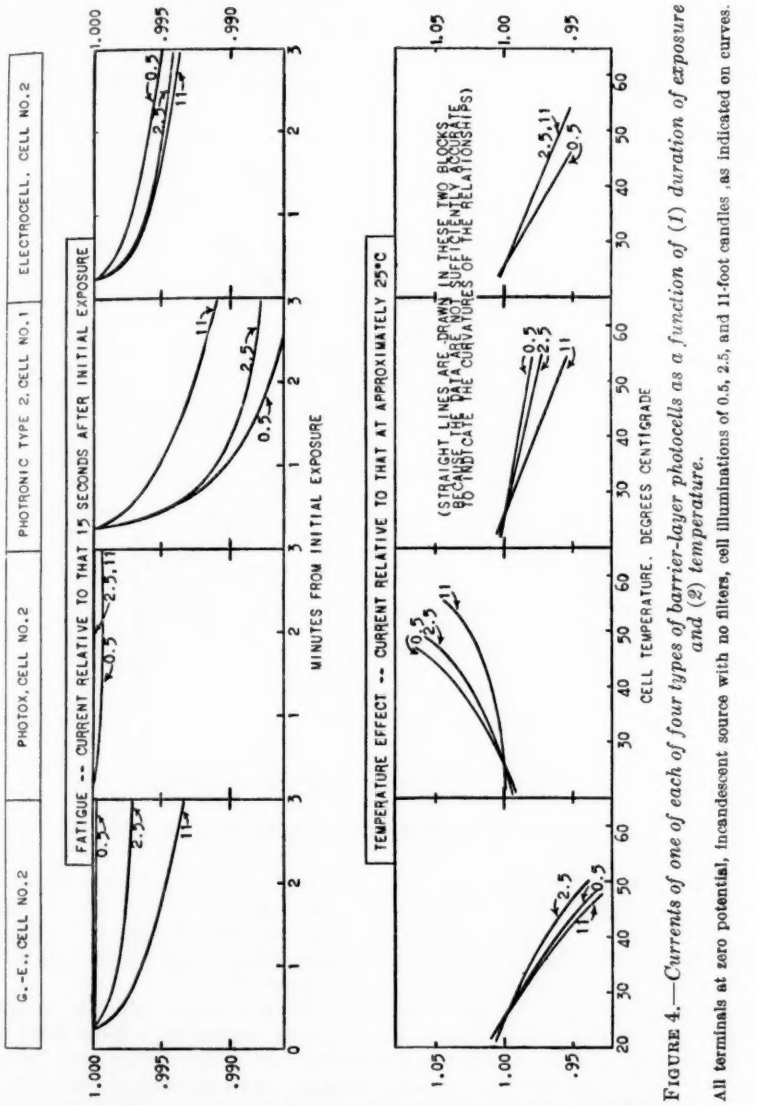
G.-E., CELL NO.2
PHOTOX, CELL NO.2
PHOTRONIC TYPE 2, CELL NO.1
ELECTROCELL, CELL NO.2
FATIGUE -- CURRENT RELATIVE TO THAT 15 SECONDS AFTER INITIAL EXPOSURE
MINUTES FROM INITIAL EXPOSURE
TEMPERATURE EFFECT -- CURRENT RELATIVE TO THAT AT APPROXIMATELY 25°C
(STRAIGHT LINES ARE DRAWN IN THESE TWO BLOCKS BECAUSE THE DATA ARE NOT SUFFICIENTLY ACCURATE TO INDICATE THE CURVATURES OF THE RELATIONSHIPS)
CELL TEMPERATURE, DEGREES CENTIGRADE

FIGURE 4.—*Currents of one of each of four types of barrier-layer photocells as a function of (1) duration of exposure and (2) temperature.*

All terminals at zero potential, incandescent source with no filters, cell illuminations of 0.5, 2.5, and 11-foot candles, as indicated on curves.

IV. AUTHOR'S EARLIER REFLECTOMETERS

The first reflectometer built by the author was the 0°,45° visual reflectometer, illustrated in figure 5 [25]. The outline of the instrument is shown, and the lines of sight and directions of movement of the lamp are indicated. The two surfaces to be compared, mounted

at opposite ends of the instrument, are illuminated by the source, which may be moved along the supporting rods to vary the illuminations upon them. These surfaces are viewed in a direction approximately 45° from normal, and, with the aid of a pattern mirror, they are seen in photometric juxtaposition. The observer balances their brightnesses in the pattern-mirror field by shifting the source and makes settings for equality of brightness. The 0°,45° luminous apparent reflectance ($A_{0°,45°}$) of a test surface relative to that of a comparison surface is indicated on a scale which moves with the

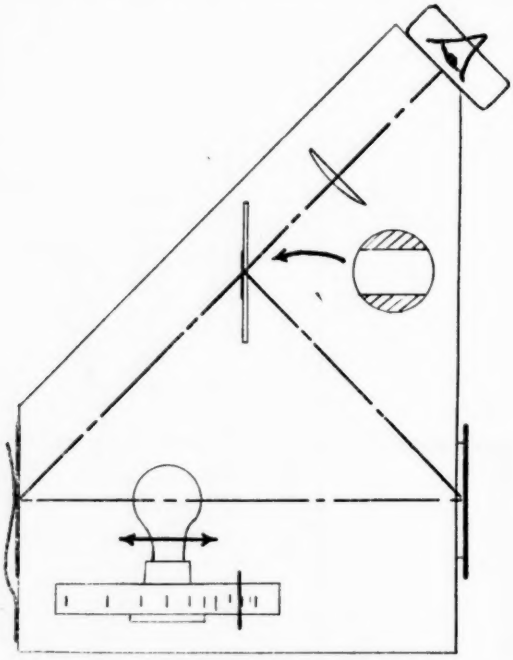

FIGURE 5.—*Null-method visual reflectometer.*

source. Comparison of sample and standard is made by the substitution method.

The Photox reflectometer was designed, as noted above, as a null-method photoelectric instrument making measurements of $A_{0°,45°}$ (equivalent to $A_{45°,0°}$). Previous descriptions of this photoelectric adaptation of the visual reflectometer being incomplete [6, 26], a short account is included in the present paper.

Figure 6 gives the plan of the Photox reflectometer designed especially to measure $A_{0°,45°}$ of vitreous enamels. The lamp, its direction of motion, the positions of the test and comparison surfaces, and the directions of "view" are the same as in the visual reflectometer just described. The comparison and test surfaces are illuminated along directions near the perpendicular by light from the movable lamp between them. Two 5-diopter, 3-in. diameter, plano-convex lenses are used to direct light reflected from each surface to its corresponding photocell. A shutter varies the proportions of light reaching the two cells by diaphragming at will either beam. The instrument is

housed in a rectangular metal box—over-all dimensions, 44 by 40 by 23 cm.

As stated in section III, the two Photox cells are connected with different polarities to the terminals of a galvanometer which is deflected when currents generated by the two cells do not balance. A 60-watt, pear-shaped, Mazda lamp, operating on a 110-volt supply to give a color temperature of approximately 2,840° K is used as source of illumination. With MgO in the test position and a white

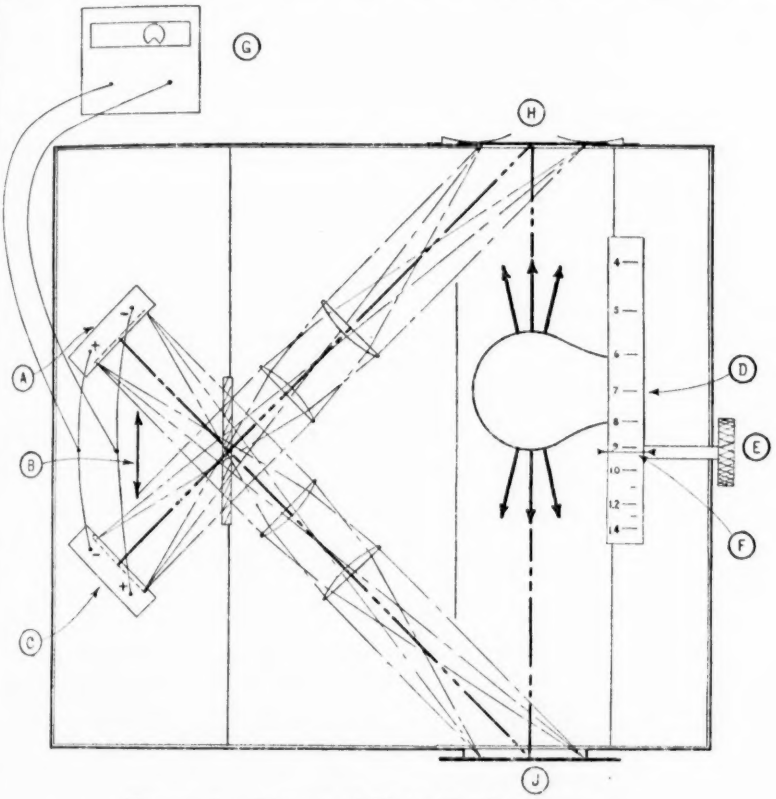

FIGURE 6.—*Diagram of Photox 0°,45° reflectometer.*

A, test Photox cell; *B*, shutter; *C*, comparison Photox cell; *D*, lamp and scale attached; *E*, knob to move lamp and scale; *F*, index; *G*, galvanometer; *H*, comparison surface; and *J*, test surface.

porcelain surface in the comparison position, the illumination upon each Photox cell, when balanced, is roughly 2 foot-candles. The box-type galvanometer used responds with 1-mm deflection to a current of 0.02 microampere through its 1,000-ohm coil.

The dimensions of the lamp and the enclosure in which the lamp operates are the same in the Photox instrument as in the visual instrument. Since the directions of view are also the same, the reflectometer scales used with the visual and Photox instruments are identical.

Settings for $A_{0°,45°}$ are made in the same manner as with the visual instrument. A standard of known value is placed in the test position; the scale is set for the luminous apparent reflectance of this

standard; and the shutter is then moved to bring the galvanometer to zero. With the instrument thus adjusted, the surface to be tested is substituted for the standard; and now the lamp with scale is moved to the new position giving null deflection of the galvanometer. Luminous apparent reflectance is then read from the scale.

In addition to its use for (1) the standard porcelain-enamel reflectance test [49], the Photox reflectometer has been employed (2) to test paints for compliance with specified minimum acceptable values of $A_{0°,45°}$ [11], (3) to measure the opacity of paper [37], (4) to measure the cleaning power of soaps and detergents [8], and (5) to compare the lightnesses of surfaces [39].

The two paths from the illuminated surfaces to the corresponding photocells cross at a position (shaded area in fig. 6) where it was originally planned to insert spectral filters. It may be seen in figure 1, however, that the Photox cell responds but weakly to both the blue and red regions of the spectrum; hence the reflectometer with Photox cells is not readily adaptable to either tristimulus colorimetry or abridged spectrophotometry, both of which require the use of source-filter-photocell combinations of appreciable sensitivity in the end regions of the visible spectrum. Moreover, because of unsatisfactory compensation for fatigue and temperature changes of cells, it is not feasible to substitute in the Photox reflectometer one or the other types of barrier-layer photocells which can be used with spectral filters. It might be possible to modify the instrument so that it would operate satisfactorily with the GE or other type of cell; but rather than do this, attention was directed to the development of a reflectometer having a greater number of uses (among them the measurement of specular gloss) and of such design as to hold the effects of undesirable photocell behavior to a minimum.

V. THE MULTIPURPOSE REFLECTOMETER

1. PLAN OF INSTRUMENT

In figure 7 is a diagram of the multipurpose reflectometer with a partial elevation through Q–Q to show the path of the gloss beam[5] to and from the gloss surface. The lines indicating both the centers and the edges of the light paths from the source to the respective photocells are heavy. The positions of all elements necessary for the operation of the instrument are shown. The elevated part of the gloss beam between the mirrors, F and I, is omitted in the plan but is shown in the partial elevation.

The instrument, as has been noted, is designed to operate according to a null method. Light from the single source is divided into two paths, each of which ultimately reaches a barrier-layer photocell. The two cells are connected, with polarities opposing, to the terminals of the galvanometer, giving the current-balancing circuit described above. The paths followed by the two beams are purposely geometrically different so that different operations may be performed with them. Light diverges from the filament of the projection lamp, C, and passes through a round window in the aluminum insulating shield, B. Beyond this shield, the beam may pass through one of

[5] "Gloss beam" is used hereinafter to designate the pencil of light which is separated from the entrant beam by the small aluminum mirror, F, and which ultimately reaches the stationary photocell, N. "Gloss photocell" is used to designate this photocell and "gloss surface" to designate the surface, H, in position to receive the beam at 45° and reflect it at −45° along the path toward the gloss photocell.

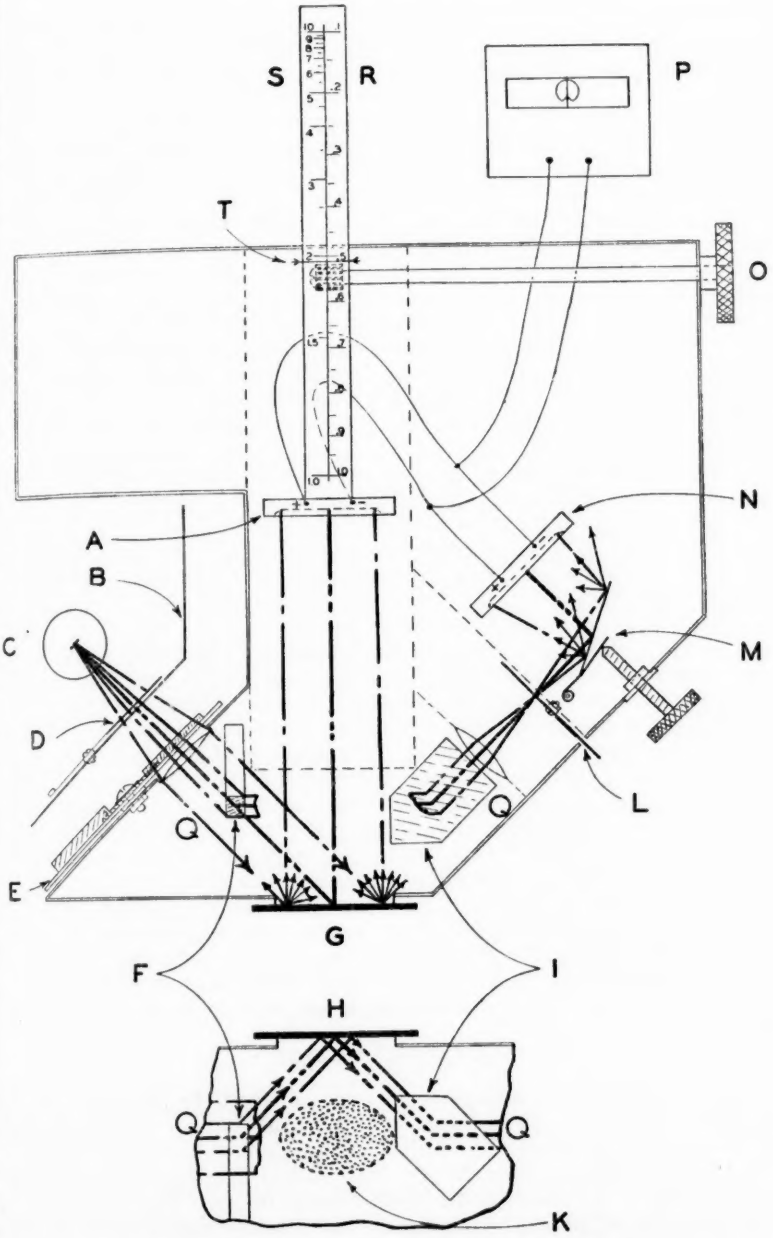

FIGURE 7.—*Diagram of multipurpose reflectometer.*

A, reflection photocell; *B*, aluminum shield; *C*, lamp; *D*, shutter; *E*, filter disk; *F*, small mirror which divides beam; *G*, reflection surface; *H*, gloss surface; *I*, aluminum mirror; *K*, cross section of area through which light passes between reflection surface and reflection photocell; *L*, disk containing gloss apertures; *M*, screw and semidiffusing reflector; *N*, gloss photocell; *O*, knob to move cells and scales; *P*, galvanometer; *R*, reflection scale; *S*, gloss scale; and T, index. Elevation through *Q*–*Q* at the bottom shows how light is directed up to the gloss surface, *H*, from the plane of the other beams of the instrument below.

several spectrally selective filters on a disk, *E*, and reach the collimating lens mounted in the wall of the instrument housing. The approximately parallel beam leaving this lens then proceeds, in large part, to the vertically placed reflection surface,[6] *G*, on which it is incident at 45°. The reflection photocell, *A*, to which the scales are attached, "views" the reflection surface from a variable distance.

The plane mirror, *F*, intercepts a small part of the cylindrical beam and reflects it upward to incidence at 45° on the horizontally placed gloss surface, *H*. The light reflected by this surface at the angle of mirror reflection, −45°, strikes mirror *I*, which is in the same plane as mirror *F*. The center of this gloss beam is thereby returned to the horizontal plane and passes through a lens and "gloss aperture", where an image of the source is formed. Behind this aperture is the semidiffusing reflector, *M*, adjustable in its angular position to control the fraction of light directed from it to the gloss cell, *N*. Several different apertures in a disk may be interchanged to vary the spread [30] of the light in the gloss beam passed toward the gloss cell for measurement.

Two scales are ruled on the arm attached to the movable reflection cell, one for reflection, *R*, the other for gloss, *S*. Stray light which might register on the photocells is reduced to a minimum by painting interior surfaces of the instrument a dull black, by mounting the movable reflection cell in a tunnel, and by dividing the instrument interior into compartments separated by the sheet-metal partitions indicated by light dotted lines in figure 7.

Because test samples may be introduced in either the gloss or the reflection beams and because the gloss beam may be extended above the instrument into attachments for performing additional operations, the multipurpose reflectometer will measure a number of different quantities. For every operation except that of measuring contrast gloss, one beam is made the comparison beam, the other the test beam. Whenever $A_{45°,0°}$ is measured, the comparison surface, which must be permanent in its specular reflection, is placed in the gloss position. Conversely, a surface for which the value of $A_{45°,0°}$ is stable is inserted in the reflection position whenever the gloss beam is used for the specimens to be tested. The comparison specimen, whether it is a mirror or a dark-gray porcelain-enameled plaque, need not be calibrated. The calibrated standard is always one which may be inserted in the instrument in the same position in which the samples are thereafter exposed for measurement, as is customary in all substitution methods.

2. CONSTRUCTION

Three multipurpose reflectometers are in use at the National Bureau of Standards, and some of the more important details [7] of construction of these are given here. The reflectometer shell and interior partitions are of sheet metal, mainly 20-gage galvanized iron painted inside with matte black and outside with black-crystal finish. The reflectometer body is 40 cm wide and 16 cm high. The relative sizes of the compartments and elements within the instrument are rendered accurately in

[6] Surfaces inserted in this position, *G*, may be measured for $A_{45°,0°}$. This position of the test samples hereinafter termed the "reflection position" to differentiate it from the position in which samples are placed for gloss measurement, *H*. The beam is termed the "reflection beam," and the viewing photocell, *A*, is termed the "reflection photocell."

[7] The detailed plans used in building these instruments may be consulted in the Colorimetry and Spectrophotometry Section, National Bureau of Standards.

the diagram, figure 7. The dimensions of the different photocells which may be used are given in table 1.

Concentrated-filament projection lamps of 100 to 400 watts may be used. The ventilated lamp housing must be thermally insulated from the body of the instrument, but the lamp filament must not move relative to it. In some cases the lamp socket and lamp housing have been mounted on a U-shaped bar attached rigidly through insulating washers to the instrument body. In one case, the body, insulating shield, and lamp socket were mounted on a rigid board which does not readily conduct heat.[8] However, it has been found that even though the lamp socket be rigidly located relative to the body, movement of the lamp in its socket will sometimes take place during operation. Such movement has been found in both the medium-screw-base and medium-prefocus-base sockets which have been tried. Trouble is most likely to occur during the warm-up period, when the instrument has just been turned on and heating causes changes in the parts.

Simple, double-convex lenses 42 mm in diameter are used (10 diopters for the collimating lens and 20 diopters for the gloss-beam lens). The spectral filters employed are 2 in. square. The small mirror, *F*, in the entrant beam is of chrome-aluminum, about 15 mm square, deposited by evaporation on the end of a thin strip of glass. The mirror, *I*, is large, so that its back side will block all light proceeding from the reflection surface toward the gloss photocell. This mirror may be of electrolytically brightened sheet aluminum, chrome-aluminum deposited by evaporation, or other nonselective mirror material. The small circular opening in the disk containing gloss apertures is used for specular-gloss measurements. It is 6.2 mm in diameter and provides an angular spread [9] of the gloss beam of 11.7°. For measurements of quantities other than specular gloss, bloom, and sheen, a large circular opening 25 mm in diameter is used to provide for the maximum angular spread (about 22°) possible with the present lens system. Three openings of this large size are used; two hold "neutral" filters. The 7 by 5 cm semidiffusing reflector beyond the disk is of electrolytically brightened sheet aluminum; however, a surface painted with aluminum varnish will serve the same purpose.

Both of the instrument openings upon which samples are mounted are oval, 7 cm long and 5 cm wide. The samples are placed against a brass collar raised 7 mm from the shell of the instrument to keep the instrument body and the samples from contact over extended areas. Almost the whole reflection opening is filled by the incident beam; consequently samples for measurements of $A_{45°,0°}$ are required to have flat areas at least 7 by 5 cm (unless the special device for small areas is used). The gloss beam, on the other hand, covers only a diamond-shaped area 3.8 cm long and 2.5 cm wide in the center of the gloss opening, but specimens to be tested must have a somewhat larger flat area to hold against the 7- by 5-cm elliptically shaped brass collar.

Several auxiliary features may be noted. The clamp which holds the samples during measurement is attached to the end of a spring-bronze arm through a ball and socket so that it will hold specimens of almost any shape firmly in position. It may be used interchangeably over the gloss and reflection openings. Also interchangeable is the

[8] The author is indebted to I. A. Balinkin, of the University of Cincinnati, for suggesting this second method of assembling a reflectometer.

[9] For an explanation of what is meant by the spread of a gloss beam see reference [30].

movable guide which determines the location of the test piece of the area that is measured. The work of the Porcelain Enamel Institute Committee on Standardization of Tests furnished an example of the use of this guide. It was necessary to measure the specular gloss of the same area of each test piece before and after treatment. By leaving the guide locked in position while etching or abrading a sample it was always possible to remeasure after treatment the exact area initially exposed.

The knob to move the reflection cell, the lever to open the shutter, and a key to reduce the response of the galvanometer are located close together on the rear right side of the instrument, where they may be easily reached by the right hand. A reading lens and mirror enable the operator to read the scales while seated in front of the instrument. The semidiffusing reflector is turned by a thumbscrew conveniently placed in the position indicated by figure 7. A thumb nut on the shank of this screw enables the operator to lock the reflector in any position desired.

Except when the reflectometer is used for abridged spectrophotometry or with the small rectangular GE photocells, a galvanometer with which one may detect a current of 0.003 microampere is suitable. If, however, the smaller rectangular cells are used with a projection lamp of less than 400 watts, the galvanometer must respond visibly to a current of 0.001 microampere. For abridged spectrophotometry, a galvanometer which will detect with certainty the presence of a current of 0.0001 microampere is needed because of the necessarily low transmission of some of the filters used; the coil of the galvanometer should have a resistance of about 1,000 ohms.

3. ATTACHMENTS FOR SPECIAL OPERATIONS

The first of the several attachments built to adapt the instrument to special problems is a stand (not illustrated) to lift the reflectometer about 8 in. above the table top and mount it in a vertical instead of a horizontal position so that dry powders or opaque liquids in open pans may be introduced for 45°,0° measurements. When the reflectometer is used in this position, the lamp mounting must be turned, because projection lamps must always be operated with base down.

Figure 8 (*A*) illustrates a device which is used with nonflat surfaces or with surfaces too small in area to fill the full reflection opening. The device consists of a simple lens (20 dipoters, 42 mm diam) which converges the incident beam to three-eighths inch in diameter at the plane of the reflection surface. During the use of this attachment, a major portion of the incident beam departs significantly from 45° incidence. Since, moreover, nonflat surfaces and surfaces too small to measure in the usual manner are difficult to accurately position for measurement, the apparent reflectances obtained with this attachment are not as accurate as those obtained in the usual manner.

To measure specular gloss at angles other than 45°, attachments of the type shown in figure 8 (*B*) are mounted on top of the reflectometer and test specimens are placed upon them. By changing the dimensions and the angles of the two mirrors, the type of device may be designed for specular-gloss measurements at any angle desired. Measurements at both 60°, figure 8 (*B*), and at 75°, figure 12, have been made with the multipurpose reflectometer. Used with the small gloss aperture, the 60° attachment has been found to give gloss values

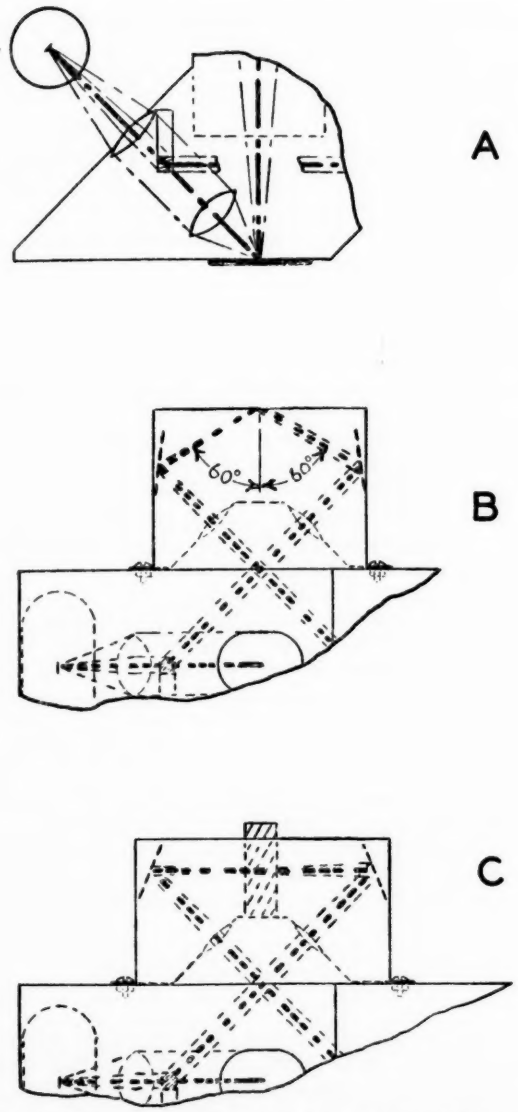

FIGURE 8.—*Three reflectometer attachments for special functions.*

A, For approximate values of $A_{45°,0°}$ of nonflat surfaces and surfaces of small area; *B*, for 60°,−60° specular gloss; *C*, for transmission.

of painted surfaces in fairly good accord with those derived according to the ASTM Tentative Method of Test for Specular Gloss of Paint Finishes [1, 30].

For transmission, figure 8 (*C*), the gloss beam is directed horizontally through the top of the same type of device. Clear liquids in glass cells and clear solids with polished parallel faces are then inserted for measurement.

VI. PREPARATION OF SCALES AND CORRECTION CURVES

1. PREPARATION OF THE SCALES

With the multipurpose reflectometer every setting on an unknown sample is made by moving the reflection cell to a position at which the current it generates balances that generated by the gloss cell. The scales of the instrument are attached to the reflection cell and pass under a ruled index line in the manner indicated in figure 7. Roughly, the gloss-scale settings vary inversely as the square of the distance between the reflection surface and the reflection cell, and the reflection-scale readings vary directly as the square of this distance.

For the first multipurpose reflectometer, direct-reading scales were prepared using as guides instrument settings on a series of porcelain-enamel plaques of known luminous apparent reflectances. For subsequent reflectometers, printed duplicates of the scales drawn for the first instrument have been used. Although these later instruments have not duplicated the first device in every detail, it has nevertheless proved practical to use the printed duplicate scales and then prepare for each instrument the separate scale-correction curves. The scale errors which must be corrected are, for many conditions, not large. The paragraphs following describe the preparation of the first scales and of subsequent scale-correction curves.

A centimeter scale was mounted on the scale arm of the first multipurpose reflectometer in such a position that it indicated the distance from the reflection surface to the reflection-cell face. Null settings were then made on each of the porcelain-enamel plaques of a previously measured white to medium-gray series, and the values of $A_{45°,0°}$ of these plaques were plotted against the distances, giving the dots in figure 9.

The circles in this figure were obtained from a photometric equation which nearly fits the experimentally determined scale. The fraction of the total flux from one circular disk radiating according to Lambert's law which reaches a second disk of equal radius, both disks being perpendicular to the line joining their centers, is, according to Walsh [55],

$$\frac{F_2}{F_1}=\frac{1}{2r^2}\left[2r^2+d^2-d\sqrt{4r^2+d^2}\right],$$

where r is the radius of the disks, d their distance apart, F_1 the flux radiating from the face of the first disk and F_2 the flux incident upon the second disk. For an instrument fulfilling the ideal conditions, this equation would serve for spacing the rulings on the scales;[10] in the present case it proved valuable as a check against the experimental calibration. Setting $r=2.5$ cm, a series of values of F_2/F_1 were computed relative to that at 33.8 cm (the distance corresponding to a scale setting of 1.0). The reciprocals of these numbers were plotted in figure 9 as a function of d. The reflection-scale curve was then drawn through the experimentally determined dots, using the

[10] Failure of this function to apply to the actual instrument arises, in major part, from the presence of stray light, which it is impossible to eliminate entirely, and, to a lesser degree, from the fact that the reflection surface and, in some cases, the reflection photocell are not circular. This failure of the scale to fit Walsh's function is noted in the study of a multipurpose reflectometer by the Institute of Paper Chemistry [33]. They mistakenly assumed in their study that it was intended to have the reflectometer scale fit such a photometric relationship. Actually, in using Walsh's equation, it was intended only to verify in an approximate manner the experimental calibration for interpolation purposes.

circles to guide in locating the interpolated and extrapolated parts of the curve.

The curve for gloss, also plotted in figure 9, is the locus of points whose ordinates are reciprocal to the corresponding ordinates of the reflection-scale curve. In measuring gloss, it will be remembered, test sample and comparison surface positions are reversed, hence the inverse relation of the gloss scale and the reflection scale.

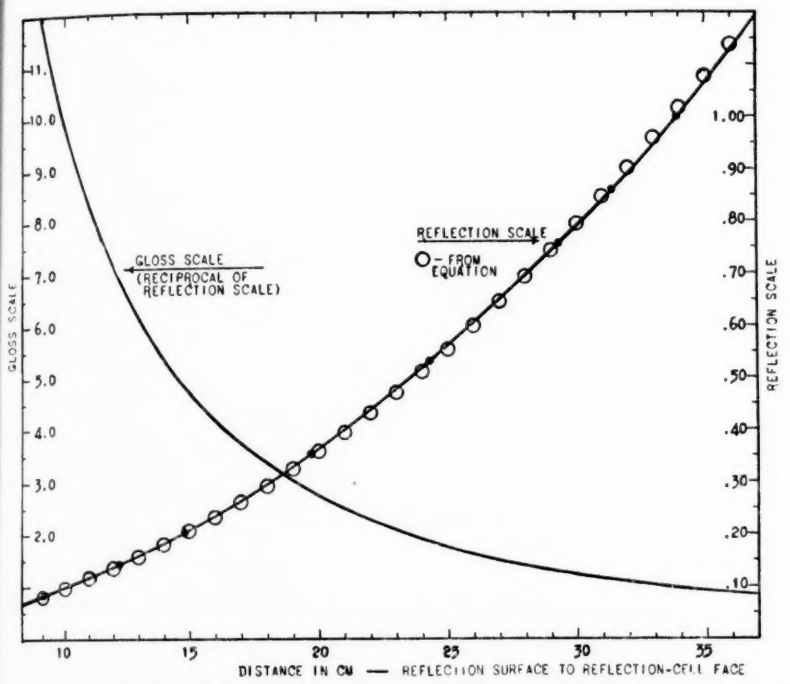

FIGURE 9.—*Small-scale copy of the reflection- and gloss-scale calibration curves of one multipurpose reflectometer.*

The circles are relative values of F_1/F_3 calculated from Walsh's equation with r=2.5 cm.

The direct-reading scales were ruled from a carefully prepared enlargement of figure 9. The reflection scale extends from 0.10 to 1.00 and is convenient because of the fairly uniform, open spacing of the scale intervals, evidenced in figure 9 by the lack of a marked change of slope of the corresponding curve. The gloss scale extends from 1.00 to 10.0, but the scale intervals are not so uniformly spaced;[11] in fact, the close spacing between 5.0 and 10.0 makes it often advisable to use a scale setting between 4.0 and 6.0, instead of 10.0, as the 100 percent setting for transmission measurements. From the carefully ruled pair of direct-reading scales, a zinc etching properly reduced in size was made, and from this etching the scales used in the instruments have been printed.

[11] It will be found that $-\log_{10}T$, into which transmission (T) is frequently transformed, is more nearly a linear function of scale distance than is T.

2. CORRECTION CURVES

Minor mechanical differences in construction and differences in the behavior of different pairs of photocells cause variations in the photometric calibrations of instruments. Ideally, a new calibration should be prepared and a new pair of scales ruled for each reflectometer built. Preparing new scales is, however, difficult and tedious. It has proved practical merely to install in each new device a printed duplicate of the first scales and then prepare scale-correction curves taking account of the photometric differences between the original and the new reflectometer.

An account of the preparation of one set of these correction curves is given below. These correction curves are shown in figure 10 for the reflection scale and in figure 11 for the gloss scale. Arbitrarily, the corrections were made zero for reflection-scale settings of 1.00 and gloss-scale settings of 5.00. The correction curves give the amounts which must be added to or subtracted from the scale readings to give accurate relative values of apparent reflectance and specular gloss.

In general, apparent reflectance and gloss are each measured at several different levels, and for each level a separate scale-correction curve is required. The "full scale" curve shown in figure 10 is, for example, used to correct settings for gray and white surfaces having values of $A_{45°,0°}$ between 0.10 and 1.00. The curves labeled, "Scale$\times$ 0.1" and "scale$\times$0.01" are used to correct settings obtained after the instrument has by suitable adjustment been prepared to measure dark-gray surfaces giving values between 0.10 and 0.01 and of black surfaces giving values between 0.01 and 0.001, respectively. The curve labeled "scale$\times$0.5" is used for settings at an intermediate level.

For gloss or transmission measurements, both of which are made on the gloss scale, the correction curves (fig. 11) are identified by the apparent reflectances of the comparison surfaces used. The middle level, for which the surface has a value of $A_{45°,0°}=0.011$, includes most of the specular-gloss values measured.

To understand why the correction curves of figures 10 and 11 change from level to level, one must realize that there is stray light present within the interior of the instrument and that some of it is directed to the reflection photocell by surfaces within the instrument interior which are not perfectly absorbing and by dust and dirt. The amount of stray light reaching the reflection cell is proportionately greater when dark samples are in the reflection position, as illustrated by the larger corrections of the curves for low-level measurements.

To prepare the reflection-scale correction curves, settings were made on porcelain-enamel plaques previously subjected to careful measurement for 45°,0° luminous apparent reflectance; to prepare the gloss-scale curves, "neutral" filters of known luminous transmission were used. From the group of calibrated specimens available, several settings at each level were made. From each setting, the correction required to give the proper known value was computed and plotted on one of the pieces of coordinate paper from which figures 10 and 11 were drawn. There were relatively few points for each level, however, and therefore trustworthy correction curves could not be drawn because of uncertainty regarding the courses of the curves between the plotted points. To interpolate between the points representing the known amounts of correction, and to extrapolate at the ends of the curves,

pairs of settings were made with a piece of clear glass having a transmission of 0.924 alternately introduced into and removed from the gloss beam to provide a photometric interval of known magnitude. All the scale ranges ordinarily used were covered with pairs of settings, and the departures of the scale-assigned ratios from 0.924 were the

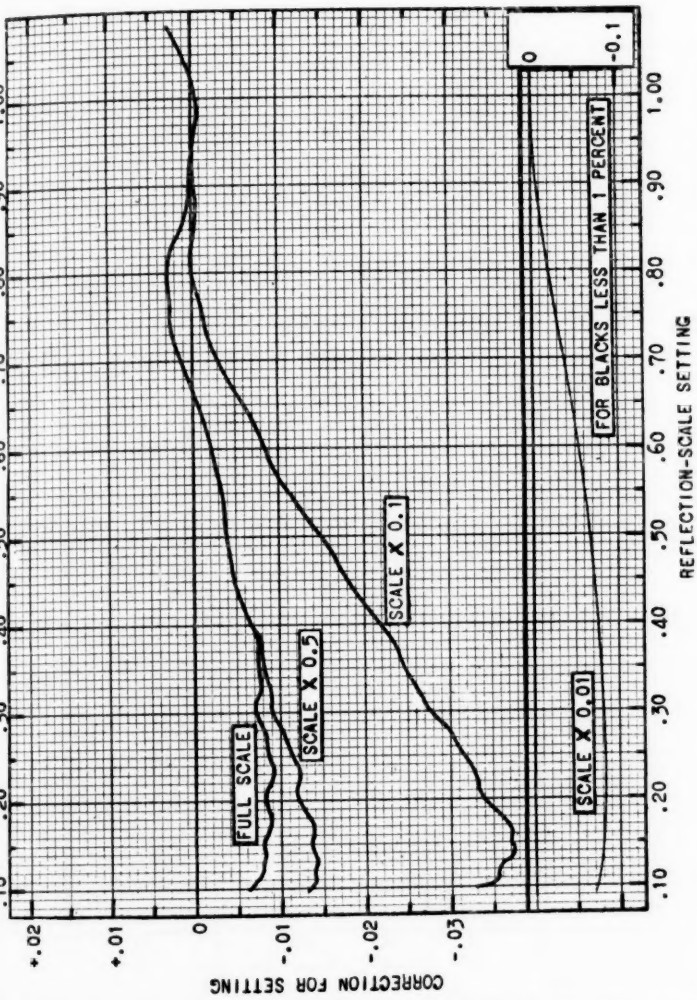

FIGURE 10.—*Corrections applied to the reflection-scale settings of one instrument when the values of $A_{45°,0°}$ of the samples measured are roughly 1.0, 0.5, 0.1, or 0.01 times settings.*

bases of corrections for interpolating and extrapolating the correction curves. As the semidiffusing reflector was adjusted to give different scale settings in this work, the samples in gloss and reflection position were frequently changed so that they were always similar in reflecting characteristics to the samples met in actual operation of the instrument in the same scale range. Approximately 30 additional points for each correction curve were obtained by making settings with this piece of clear glass.

Although the resulting scale-correction curves in figures 10 and 11 apply to only one instrument, the curves and the description of the manner in which they were obtained may be helpful for preparing similar ones. The correction curves of other instruments which have

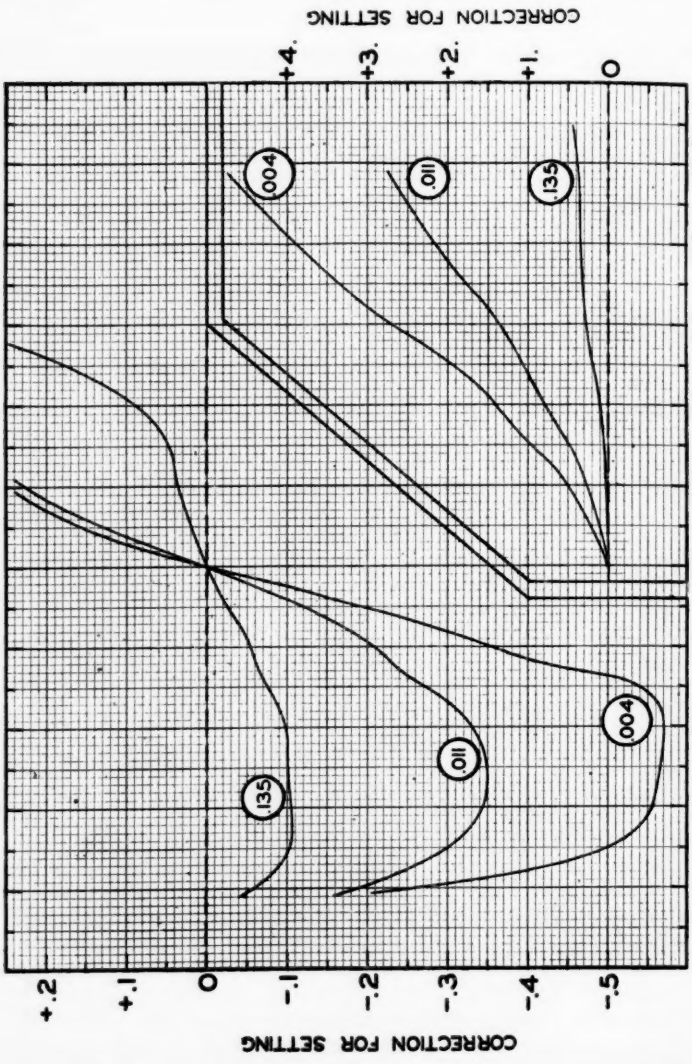

FIGURE 11.—*Corrections applied to the gloss-scale settings of one instrument when the $A_{45^\circ,0^\circ}$ of the comparison surface is 0.135, 0.011, or 0.004.*

scales printed from the same etching should have irregularities in the same places as those in figures 10 and 11, because these irregularities (though not the general shape of the curves) are thought to result chiefly from inaccuracies in the preparation of the original drawing.

VII. ELIMINATING OR MINIMIZING ERRORS

Eighteen potential errors in multipurpose reflectometer measurements are listed in table 2, together with the evidence by which the presence of each is detected and the procedure employed to minimize or eliminate each. The 18 are divided into a group of 12, identified by inconstant operation of an instrument, and a group of 6, the presence of which can only be established by the failure of one instrument to check results from another. Since the cause, the evidence of presence, and the cure for each of the 12 errors of inconstancy are indicated in the table, no further discussion of them is given.

TABLE 2.—*Errors in multipurpose reflectometer measurements, their causes and control*

Evidence of presence of error	Cause of error	To minimize or eliminate the error
A. ERRORS EVIDENCED BY INCONSTANT OPERATION OF SINGLE INSTRUMENT		
FROM CHARACTERISTICS OF THE PHOTOCELLS		
1. Change of settings with temperature of instrument.	Change of photocell current with temperature.	Allow instrument to warm up to equilibrium and check with standard frequently to detect drift.
2. Galvanometer drift after opening shutter.	Change, with time, of current from one photocell relative to that from the other (fatigue).	Use photocells paired for equal rate of drift and thus eliminate residual drift.
3. Galvanometer response to change of line voltage.	Change with source intensity of current from one photocell relative to that from the other.	Use photocells paired for like changes of current with identical changes of illumination.
4. Persistent failure of instrument to reproduce readings made shortly before; galvanometer drift.	Failure of contacts within photocells.	Renew electrical contacts within cells, or replace cells.
FROM DESIGN OF THE INSTRUMENT		
5. Galvanometer response to movement of a light past cracks and openings in the instrument.	Light leakage	Make housing light tight, or use instrument in a darkened room.
6. Galvanometer response to pressure on, or movement of, instrument during a setting.	Lack of structural rigidity	Build instrument rigidly; handle carefully during use.
7. Erratic operation	Dirt on optical parts	Clean parts affected.
FROM CHARACTERISTICS OF THE SAMPLE		
8. Galvanometer response to change of line voltage only when instrument beams have markedly different spectral composition.	Marked spectral difference of samples in two beams.	Operate source at constant voltage when beams have markedly different spectral composition.
9. Change of instrument reading with change of area of surface exposed.	Nonuniformity of surface of the sample in the quality being measured.	Designate area of surface measured.
10. Change of instrument reading with wobble of surface over opening.	Nonflatness of surface of sample.	Flatten surface or designate exact position during measurement.
11. Change of instrument reading with rotation of sample surface.	Variation of apparent reflectance of surface with rotation in its own plane.	Make and average four readings of sample rotating it 90° between each pair of readings.
12. Change of reading with exposure of sample to light, time, humidity, or other treatment.	Impermanence of characteristics of sample.	Treat sample so affected with care and give history prior to measurement.

TABLE 2. *Errors in multipurpose reflectometer measurements, their causes and control*—Continued

Evidence of presence of error	Cause of error	To minimize or eliminate the error
B. ERRORS IDENTIFIED BY USE OF SEPARATE INSTRUMENTS		
13. Failure of reflectometer to check accurate results from separate instruments.	Inaccurate scales	Prepare and use scale-correction curves following instructions.
14. Do	Inaccurate calibration or change of standard.	Remeasure standard.
15. Failure of reflectometer to check accurate results from separate instruments (frequently appears when results are compared with those from instrument of different type).	Inexact duplication of specified directional conditions of measurement.	Examine angular conditions of measurement of both instruments involved. (Do not expect accurate duplication of results if there are differences.)
16. Failure of reflectometer to check accurate results from separate instruments. (Penetration of light is often visible at edges of sample.)	Loss of light by lateral passage after penetration into translucent sample.	Measure on instrument having negligible penetration loss. (See text.)
17. Failure of reflectometer to check accurate results from separate instruments.	Failure of spectral response of source-filter-photocell combinations to duplicate those required.	Use standards spectrally similar to samples measured.
18. Do	Fluorescence of samples	Samples must be measured on instrument not subject to fluorescence error.

Errors of the last six types are harder to identify and eradicate. Scale errors, type 13, are handled by the procedure involving preparation and use of scale-correction curves, which has just been described. Type 14 does not require extended consideration here because references to the different primary standards and to suitable secondary standards are part of the study, described below, of applications of the multipurpose reflectometer. The multipurpose reflectometer itself measures only relative values and is therefore dependent for accuracy upon the standards used for the different quantities it measures.

Disagreements attributable to error 15 appear when two instruments, which are geometrically the same according to their descriptions, possess undisclosed geometric differences. One must, of course, expect lack of agreement in results from two instruments of disclosed differences; for instance, a device designed to measure $A_{45°,0°}$ will in general give results which differ from those by another designed to measure $A_{\text{diffuse},0°}$, or a device to measure 60° specular gloss will in general give results which differ from those by any device measuring 45° specular gloss.

This error 15 appears most frequently in gloss studies, because gloss measurements always involve directions adjacent to or including the direction of mirror reflection for which the apparent reflectance of most surfaces changes markedly with small changes of angle.[12] To describe adequately the geometry of a gloss measurement, one should give not only the central directions of illuminating and viewing (as, for example, 45° and −45° for specular gloss with the multipurpose reflectometer) but he should give in addition the spreads [30] of the beams. These latter quantities give the amounts of departure from the central directions of illuminating and viewing which the gloss measurement encompasses. The total spread, for example, of

[12] For illustrations of these changes see the goniophotometric curves in references [27] and [43].

the multipurpose gloss beam with small aperture is, as was stated above, roughly 11.7°.

If two gloss instruments are identical in central directions and spreads and if the gloss beams are accurately centered about the central directions, the devices should give identical results. However, a small difference in the geometry of the devices, which might result merely from the inexact construction of some part in one, may cause significant disagreement between results given by them.

In connection with errors involving the geometry of measurements, it seemed desirable to find whether the amount of light reflected in directions other than those subject to measurement might not on some occasions affect instrument settings. When, for example, a shiny black surface is exposed in reflection position, the amount of light specularly reflected into the interior of the instrument is much greater than that going directly from the test surface to the reflection photocell. It was suspected that some of the specularly reflected light might indirectly reach the reflection photocell from the walls of the instrument interior and cause the setting to be in error. To find whether such an effect existed, a shiny black porcelain-enamel plaque and a piece of matte black velvet were measured with first the goniophotometer, not subject to the error, and then with the multipurpose reflectometer. On the former instrument both were found to have a value of $A_{45°,0°}=0.004_2$; on the latter they measured 0.004_5 and 0.004_3, respectively. Considering the difficulty of obtaining accuracy in the measurement of such low apparent reflectances, one can see that any effect of gloss of test surfaces on measured values of $A_{45°,0°}$ is negligible.[13]

With further reference to errors of geometry, it should be remembered that different types of photocells have sensitive areas of different shapes and sizes. Changing the type of photocell in a reflectometer makes necessary the recalibration of the instrument by the preparation of new correction curves.

A piece of white architectural glass will furnish an example of the type of sample subject to error 16. Whenever a sample being measured in an instrument is translucent enough to permit some of the incident light to penetrate to a depth which is an appreciable fraction of the diameter of the area illuminated, part of the penetrating light will spread laterally within the sample and return to the surface outside the area illuminated. This laterally displaced light emerging from such a sample exposed in the reflectometer cannot reach the reflection photocell, because the area of the surface exposed to the photocell is only as large as the area illuminated. Because the 5- and 7-cm diameters of the elliptical opening of the multipurpose reflectometer are large relative to the depths of light penetration into most materials, translucency errors are usually small. However, this error was easily demonstrated in the case of a white opal-glass plate into which an appreciable fraction of the incident light penetrated the full 0.9 cm of its thickness. This plate, measured on the multipurpose reflectometer, was found to have a value of $A_{45°,0°}=0.909$ relative to MgO; whereas the McNicholas goniophotometer [44], in which this error is eliminated, gave $A_{45°,0°}=0.913$.

[13] Possible exceptions occur with settings at the end of the scale when the photocell is very near the reflection surface, and with settings when the converging lens described above is used to measure surfaces of small area. In each of these instances, there is possibility that specularly reflected light from the reflection surface will reach the reflection photocell to cause error.

The present discussion of error 17 will consider only its effect on measurements of luminous properties. In the forthcoming paper [29] there will be an extended discussion of this same error as it applies to photoelectric tristimulus colorimetry.

Figure 2 shows graphically the spectral disparity between the standard luminosity function and both the Photox cell with incandescent source at 2,840°K and the GE cell with green filter and incandescent source at 3,100°K. The error arising from either one of these disparities will, in general, increase as the spectral differences between the standard and samples increases. When high accuracy is required, one usually has available a standard spectrally similar to the samples and in such instances the errors are small.

Table 3 will give one an idea of the amounts of error which may result when the multipurpose reflectometer with GE cell and green filter is used to measure plaques of different color against a white plaque as standard. Values of $A_{45°,0°}$ for 10 porcelain-enamel plaques computed from spectrophotometric data [14] are compared with values for the same plaques measured with the multipurpose instrument. The reflectometer readings have been corrected for scale errors, and 0.023 has been subtracted from each of the apparent reflectance values computed from the spectrophotometric data to compensate as well as possible for the geometric differences between the two instruments. The maximum disagreement remaining is seen to amount to 0.012 (for the maize plaque) and is probably chiefly attributable to spectral disparity between the true luminosity function and the combination of source, green filter, and G. E. photocell.

TABLE 3.—*Luminous apparent reflectance* ($A_{45°,0°}$) *for 10 porcelain-enamel plaques chosen as master standards for colors of kitchen and bathroom accessories* [46, 47] *measured with* (1) *a multipurpose reflectometer using GE cell and green filter and* (2) *a spectrophotometer* [23] *by computation*

Color designations of plaques	$A_{45°,0°}$ relative to MgO for ICI illuminant *C*	
	Measured on multipurpose reflectometer with GE cell and green filter	Computed from spectrophotometric data on ICI luminosity basis
White	0.743	0.734
Bath green	.312	.318
Kitchen green	.341	.343
Orchid	.331	.325
Ivory	.587	.576
Maize	.556	.544
Bath blue	.238	.244
Delphinium blue	.165	.170
Royal blue	.045	.050
Kitchen red	.081	.080

For the measurement of samples which fluoresce appreciably, error 18 may be serious. When light from a sample which is fluorescing is evaluated by a receptor which is not corrected to respond as the human eye does, the result may differ from that which the eye would give. An instance in which the error occurred may be cited. Gibson and Keegan [20] found a certain piece of pink plastic material to be fluorescing strongly in response to yellow-green radiant energy, which

[14] The spectrophotometric curves for these plaques, together with those for the green luminosity filter, were obtained with the General Electric recording photoelectric spectrophotometer [23] by H. J. Keegan.

the green filter of the multipurpose reflectometer readily transmits. The yellow-green radiant energy was transformed by fluorescence of the sample into energy of an orange color which would be largely absorbed if directed through the green filter. Since, however, the green filter in the multipurpose instrument is located between the source and the sample, this orange light was not absorbed and the response of the cell was larger than it should have been. For this sample, the multipurpose instrument gave $A_{45°,0°}=0.220$, whereas a visual reflectometer, not subject to the error, gave $A_{45°,0°}=0.193$.

Regarding the 18 sources of error listed in table 2, we may say, in brief, that the multipurpose reflectometer must frequently be checked for possible effects of errors 1 to 12, that data must be corrected to eliminate the effect of errors 13 and 14, and that results must be examined for the possible presence of errors from sources 15 to 18, inclusive. In spite of the formidable array of sources of error, a well-built instrument used with appropriate and accurately calibrated standards and with suitable scale-correction curves will usually yield apparent reflectances in error by not more than two-tenths of 1 percent of the incident light.

VIII. APPLICATIONS OF THE MULTIPURPOSE REFLECTOMETER

1. COMPARISON OF SAMPLES VERSUS ACCURATE MEASUREMENT OF EACH, THE SUBSTITUTION METHOD

The multipurpose reflectometer has high precision and will identify small differences in apparent reflectance, color, gloss, and other properties; but it furnishes only relative, not absolute values. The solution of many problems met in practice requires, however, that the samples of a group merely be exposed for readings from the instrument and then be arranged in order according to the property in question. When this is the case and the samples of a group are similar, the last six sources of error which are so difficult to eliminate may often be ignored. Calibrated standards are not needed. A great saving of labor, in comparison with the amount required for accurate work, is therefore possible.

For quantitative results, a working standard representing the property being measured must be available. This standard should have an assigned value near those of the samples being measured. A substitution method, in which the samples are substituted for, rather than compared with, the standard, is employed. Of the two light paths the one not used for the samples being tested becomes the comparison beam; in it a single uncalibrated specimen is used.

The standard employed for an operation with the multipurpose reflectometer is seldom the primary standard of the property measured, but instead is usually a secondary or working standard which has been carefully calibrated in terms of the proper primary standard. In order to make the variety of measurements possible with the multipurpose device and to have available for any group of samples a standard of similar specifications, a large variety of working standards is needed. In the following description of the operations of the instrument, both the primary standard for each operation and the types of secondary standards most frequently employed are mentioned. These standards are noted in table 4.

TABLE 4.—*The measuring operations of the multipurpose reflectometer, some applications of each, arrangements for operation, and the standards used*

Quantity measured	Applications (The references are to papers illustrating each type of measurement, not in the majority of cases to use of the multipurpose reflectometer.)	Arrangements for operation					Standards	
		Position of sample	Scale used	Comparison surface	Gloss aperture	Spectral filters	Primary	Working
Luminous apparent reflectance, $A_{45°,0°}$.	To test paints, etc. for compliance with $A_{45°,0°}$ specifications [11]. To measure opacity and hiding power [37]. To measure cleaning power of soaps and detergents [8]. To determine lightness of surfaces (for Munsell value) [22]. To measure $A_{45°,0°}$ of blacks [25].	Reflectance.	Reflectance.	Aluminum mirror.	Large	Luminosity (green); (none with Photox cell).	MgO	White, gray, or black porcelain-enamel or other ceramic surface.
Tristimulus colorimetry (of surfaces), $A_{45°,0°}$, through three filters.	To furnish trichromatic coefficients [29]. To measure amount and indicate character of color differences [28, 29, 39]. To measure whiteness, yellowing, fading, bleaching, amount of bluing, tinting strength, etc. [53].	do	do	do	do	Green, blue, and amber tristimulus filters.	do	Porcelain-enamel or other ceramic surface similar in color and spectral character to samples.
Abridged spectrophotometry (of surfaces), $A_{45°,0°}$, through filters.	To supply approximate spectral-reflection curves [32]. To supply apparent reflectances for selected wave lengths [4].	do	do	do	do	Selected filters transmitting narrow spectral bands.	do	Ceramic plaque of known spectral 45°,0° apparent reflectance.
Specular gloss, $G_{s(45°)}$	To indicate shininess of surfaces [24]. To furnish a measure of the resistance of surfaces to abrasion, acid attack, weathering, wear, etc. [50, 51]. To classify paints and other materials for gloss [30].	Gloss	Gloss	Black plaque	Small	Luminosity (green)	Perfect mirror.	Polished black glass or surface of liquid of known refractive index.
Contrast gloss, $\frac{A_{45°,-45°}}{A_{45°,0°}}$	To determine the glossiness of surfaces of low gloss [27]. To measure papers for power to produce glare [34].	Reflectance.	Gloss or reflectance.	None	Large	do	Mirror	Matte surface measured on goniophotometer.
Bloom, $A_{45°,-45°+\delta}$	To measure the bloom of surfaces of high gloss [40].	Gloss	Gloss	Black plaque	Special	do	Perfect mirror.	Polished surface of opaque white glass.
Sheen, $G_{s\lambda(75°)}$	To measure sheen, or the shininess of surfaces at near-grazing angles [31].	On special attachment.	do	Gray plaque	Small	do	do	Polished black glass or surface of liquid.
Transmission	To measure luminous transmissions [21]. To measure abridged spectral transmissions [10]. To furnish trichromatic coefficients for transmitting specimens [29]. To supply data for chemical analyses ("chemical colorimetry") [10, 52].	do	do	Light-gray plaque.	Large	All filters (Choice depends on use).	Air, or solvent in cell.	Air, solvent in cell, standard solution, or spectral filter of known spectral transmission.

Plaques for secondary standards are, of course, chosen from stable materials. Ceramic materials, because of their relative permanence, are widely used as working standards for apparent reflectance, gloss, and trichromatic coefficients. In certain cases, surfaces of lacquer, paint, plastic, paper, or dry powder are also satisfactory as standards;

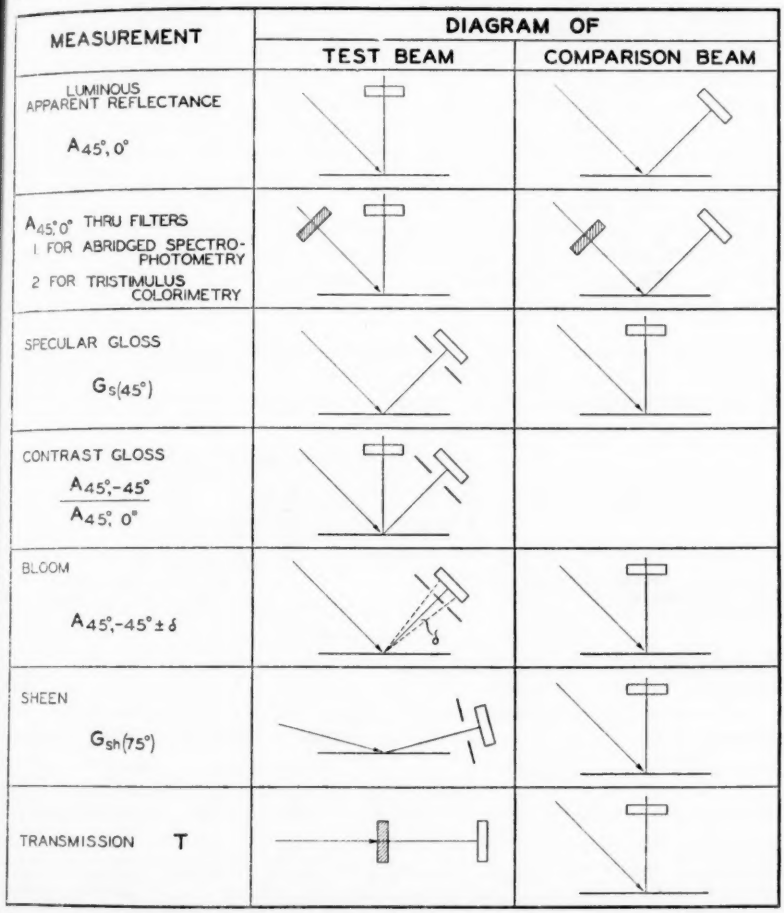

FIGURE 12.—*Different operations of the multipurpose reflectometer showing functions of both the test and comparison specimens for each operation.*

(The green filter, required with the GE cell for all measurements according to the luminosity function, is not shown.)

but specimens of any of these latter materials must be checked for permanence before use as standards. Moreover, since several porcelain enamels and ceramic tiles have been found to change color significantly with time, exposure to light, contact with water, or with other treatment, it may be said that each ceramic as well as nonceramic material must be suspected of uncertain permanence until it has proved to be otherwise. However, most porcelain-enamel plaques, blocks of opaque glass, and vitreous tiles used as standards have proved to be stable.

Considering abridged spectrophotometry and tristimulus colorimetry in separate categories, eight different measuring operations can be performed on the multipurpose reflectometer. These are shown schematically in figure 12 by the directions in which the test and comparison beams strike and leave the test and comparison samples respectively. For each of the operations there are several applications, a number of which are listed in table 4. Instances in which the measuring operations listed have been used for the purposes suggested are cited by the reference numbers following each listed application in the table. Most of these citations, however, are to cases in which the instrument employed was not a multipurpose reflectometer. The table also gives data to assist one in arranging the parts of a multipurpose reflectometer for operation and lists the primary and working standards for each operation. Table 5, by illustrating the measurement of the 45°,0° apparent reflectance of four porcelain-enamel plaques, demonstrates the form used at the National Bureau of Standards to record and reduce data for five of the eight operations.

TABLE 5.—*Form used at the National Bureau of Standards for recording and reducing multipurpose reflectometer data*

Figures in bold-face type are entered to illustrate the determination of $A_{45°,0°}$ of four porcelain-enamel plaques]

Type of measurement { x (1) 45°,0° luminous apparent reflectance
(2) 45°,0° apparent reflectance through filters
(3) 45°,−45° specular gloss
(4) 60°,−60° specular gloss
(5) Sheen (75°,−75° specular gloss), or
(6) Transmission, luminous or through filters

Samples—**4 porcelain-enamel plaques.** Settings by **RSH, 5/25/40.**
From—**Colorimetry Section, NBS.** Computations by **RSH, 5/25/40.**
NBS Test No. ---------- Checked by **DBJ.**

Standard—**Vitrolite No. 1.** Value assigned standard 0.909
Mean of corrected instrument readings of standard ..... .905
Ratio of above two values equals *adjusting factor* 1.0045

Samples	Standard	White—1	White—2	Gray	Black
NF factor				0.479	0.086
Settings	**0.909**	**0.736**	**0.809**	.2504	.1264
	.901	.732	.807	.2495	.1264
Mean (M)	.905	.734	.808	.2500	.1264
Correction	.000	+.0025	+.0028	−.0114	−.0360
Corrected M	.905	.7365	.8108	.2386	.0904
Times NF factor				.1148	.00778
Times adjusting factor	.909	.740	.814	.115	.0078

Spectral filters used—green (luminosity)

Neutral-filter (NF) factors when green filter used { Refl. scale 0.479, 0.086
Gloss scale 2.09, 11.6

To extend the 1-to-10 range of the scales of the instrument for any measurements in which the small aperture is not used, one of two neutral filters is inserted in the gloss beam by turning the disk containing gloss apertures. With the insertion of either filter, the values of $A_{45°,0°}$ measured from the scale are multiplied by, or the values of transmission or gloss are divided by, the transmissions of the filters.

For the two filters in the instrument in the Colorimetry Section, National Bureau of Standards, the transmissions are:

Nominal transmissions of "neutral" filters	Exact transmissions of "neutral" filters		
	For green tristimulus filter (giving luminosity function)	For blue tristimulus filter	For amber tristimulus filter
0.5	0.479	0.427	0.480
.1	.086	.065	.088

These two filters were used in the operation illustrated in table 5 (where they are identified by "NF factors"), in which a gray and a black plaque together with two white plaques were measured for $A_{45°,0°}$ relative to a white standard. Instead of following the procedure illustrated, the gray and black plaques could have been measured against gray and black standards, respectively, and the neutral filters would not then have been required. There are many instances, however, where these filters are necessary. In tristimulus colorimetry, for instance, selective samples are frequently encountered which cannot be measured without the use of one or both of them. An orange-colored sample, as an example, might require that the reading for amber light be made with no filter, the reading for green light be made with the "five-tenths" filter, and the reading for blue light be made with the "one-tenth" filter.

2. LUMINOUS APPARENT REFLECTANCE, $A_{45°,0°}$

In illustrating the measurement of $A_{45°,0°}$ in figure 12, no spectral filter is shown, although the green filter is required if the GE cell is used. The freshly smoked surface of magnesium oxide is the primary standard [45] to which values of $A_{45°,0°}$ usually refer. Suitable working standards are white, gray and black ceramic plaques, which, when properly calibrated in terms of the standard MgO surface, may be used for the measurement of white, moderately reflecting, and black surfaces, respectively [15].

The interest in 45°,0° luminous apparent-reflectance measurements springs from widespread use of specifications for minimum apparent reflectance of paints and porcelain enamels, from the increased use of thin applications of high-opacity coatings of porcelain enamel and the resultant need for measurements of opacity, from the interest in light-reflecting properties of paints, ceramic tiles, and other materials and from the growth of specifications for opacity, blackness, and other properties. The multipurpose-reflectometer form for the measurement of $A_{45°,0°}$ is illustrated in table 5 and shows the settings and computations for determining the apparent reflectances of four porcelain-enamel plaques. The corrections entered on the form were read from the curves in figure 10. The first and second lines of settings were taken in opposite order to minimize the effect of any drift. The reader will realize in studying this form and the data thereon that in cases where less accuracy is required, certain of the indicated steps may be omitted; conversely, in cases where the highest accuracy is required, greater care would be taken to eliminate drift by more frequent settings upon the standard.

Judd ([37] p. 311, and [37a] p. TS10) has measured the TAPPI opacity of paper, $C_{0.89}$ by using settings of $A_{45°,0°}$ employing as white backing a matte surface of $A_{45°,0°}=0.89$ and as black backing a piece of black velvet.

It may be of interest for one not familiar with the lightness scale to learn that a midgray surface diffusely reflects only about 18 percent of the incident light. Lightness varies roughly as the square root [22] of apparent reflectance, and therefore surfaces reflecting only 50 percent are sometimes called white.

3. TRISTIMULUS COLORIMETRY

Successive settings with the green, blue, and amber filters are used for each measurement of the tristimulus coefficients of a sample. Most tristimulus measurements with the multipurpose reflectometer are 45°,0° measurements of samples having opaque surfaces. For such determinations, the magnesium-oxide surface is the primary standard and secondary standards of ceramic and other materials are calibrated and used in the same manner as for measurements of $A_{45°,0°}$. In addition to the colors of opaque samples studied by 45°,0° measurements, the colors of samples viewed by light specularly reflected from them or by light transmitted through them are sometimes of interest. Tristimulus measurements of gloss and transmission with the multipurpose reflectometer will give data about these latter properties.

Tristimulus measurements may be used (1) to find the approximate trilinear coordinates of a surface color, (2) to measure the amount and direction of a color change in a specimen, (3) to measure the amount and direction of a color difference between two samples, and (4) to furnish numerical measures of whiteness and yellowness. A more detailed account of the method and its applications is being prepared for presentation in the above-mentioned, forthcoming paper [29].

4. ABRIDGED SPECTROPHOTOMETRY

Abridged spectrophotometry is performed with filters which transmit spectral bands of more or less narrow wavelength range, and this differentiates it from tristimulus colorimetry. The instrument is capable of abridged spectrophotometry with any of the angular conditions which it employs, whether 45°, 0°, 45°, −45°, transmission, or other. The standards are those employed for other measurements having the same angular conditions. For "chemical colorimetry" the standard is an absorption cell filled either with the solvent or a standard solution of known composition.

The type of measurement made with photocell apparatus and filters isolating spectrally narrow bands is properly called abridged spectrophotometry because only a few filters (usually three to seven), and consequently only a few effective wavelengths, are used [32, 52]. Furthermore, only in rare instances do the filters restrict the spectral bands of energy employed for individual settings to the narrow wavelength ranges employed in true spectrophotometry. Spectral curves obtained by way of abridged spectrophotometry are neither complete nor accurate enough to be used for primary colorimetric specification, unless additional information concerning the spectral reflective or transmissive properties of the measured material is available. In many instances, however, an abridged spectrophotometric measure-

ment is useful because it is known that some particular property may be studied by using a single spectral range or several ranges each isolated by spectral filters. One or two wavelength regions are most commonly found to be sufficient for chemical analysis by photometric means ("chemical colorimetry") [10, 52, 58].

Several manufacturers supply spectral data for their filters [7, 9, 12]. Only rarely however (as for instance in [52]), have builders of abridged spectrophotometers published adequate data on the spectral characteristics of the filters offered for use with their instruments. Before ordering a set of filters for abridged spectrophotometry, the spectral ranges which the filters are to cover should be decided upon. The manufacturers' data on the spectral characteristics of filters should be consulted to find those best suited. Glass filters rather than dyed gelatines are generally to be recommended, because they are less subject to deterioration from wear and fading. Adjustments of spectral transmission may be made by combining different filter components and, with glass components, by grinding to suitable thicknesses. Instructions prepared by Gage [14] are useful for determining the thicknesses of glass components required to give filters having prescribed transmissions.

5. SPECULAR GLOSS, G_s

The specular gloss, G_s, of a surface is usually expressed as the fraction of incident light specularly reflected by it. The primary standard of specular gloss is thus the perfectly reflecting mirror which, however, is physically unattainable. Working standards of specular gloss may, nevertheless, be prepared and accurately calibrated. By using Fresnel's equation [24], it is possible to compute for any optically smooth, nonmetallic surface of known refractive index the fraction of the incident light which will be specularly reflected at a given angle. Polished pieces of black glass and plaques having matte black surfaces on which has been spread a layer of monochlorobenzene[15] or other volatile liquid of known refractive index are found to be suitable as specular-gloss standards.

Specular-gloss measurements are frequently used for studies of paint, ceramic, and paper products; in addition, polished metal surfaces and metallic coatings are sometimes examined because of interest in their shininess or reflecting power. Recently there has developed a tendency to associate certain angles with the specular-gloss measurement of certain materials. Ceramic surfaces, for example, are usually measured at 45°, paint and lacquer surfaces at 60°, and paper surfaces at 75°. The different angles chosen correspond to the viewing conditions giving the best gloss differentiation of each type of product.

During measurements of gloss with the multipurpose reflectometer it is necessary to reduce the intensity of the reflection beam to correspond to the reduction of the gloss beam, because surfaces of nonmetallic materials specularly reflect only 0.2 to 6 percent of the light incident upon them at 45° instead of roughly 75 percent as does the aluminum mirror used in gloss position during apparent-reflectance operations. This reduction is accomplished by using black plaques

[15] The technique of flowing monochlorobenzene onto a clean sand-blasted surface of black porcelain enamel and quickly making a setting for specular gloss was worked out by D. G. Moore, of the Enameled Metals Section of the National Bureau of Standards, and is to be described in a forthcoming publication. Such a surface has proved in practice to be a better specular-gloss standard than one of black glass, because it is perfectly clean and optically smooth.

having values of $A_{45°,0°}=0.011$ or 0.004 as comparison surfaces in reflection position. As is shown in figure 11, the gloss-scale corrections become inconveniently large when these dark surfaces are used in reflection position. It will, however, be possible to rule a new gloss scale not requiring these large corrections whenever there is a demand for it.

6. CONTRAST GLOSS, G_c

A contrast-gloss device measures the amount of light reflected specularly by a surface relative to that reflected diffusely from the same spot at the same time. If the mirrors A and B (see fig. 7) are swung out of the light paths, the reflectometer will furnish approximate relative values of

$$G_c(\text{type 1}) \equiv \frac{A_{45°,-45°}}{A_{45°,0°}}.^{16}$$

However, contrast gloss at 45° is more frequently

$$G_c(\text{type 2}) \equiv \frac{A_{45°,-45°}-A_{45°,0°}}{A_{45°,-45°}}.^{16}$$

[27, 30], or one minus the reciprocal of G_c(type 1).

There is no single primary standard of contrast gloss. Any good mirror or piece of polished black glass for which $A_{45°,0°}$ is zero will have a contrast gloss of infinity for type 1, or of unity for type 2. A working standard of contrast gloss is usually calibrated on a goniophotometer with which the ratio of the apparent reflectances for the two directions may be measured directly. A matte, white porcelain-enamel plaque is especially suitable.

Contrast gloss is generally used to describe the extent to which low-gloss surfaces depart from mattness. For instance, measurements of it correlate well with the tendency of pages of printed paper to produce glare from light specularly reflected by them toward the eyes of a reader.

Correction curves for contrast-gloss settings would be difficult to prepare. Contrast gloss is defined in terms of a ratio of amounts of reflection, whereas amount of scale correction depends chiefly upon the quantity of light passing from the reflection surface to the reflection-cell face. When suitable contrast-gloss standards are used, accurate values of contrast gloss may, however, be computed from apparent reflectances for the two directions separately measured and corrected.

7. BLOOM, G_b

No experience in the measurement of bloom has been gained at this writing. However, it should be practicable to develop a control method in the following manner. A gloss aperture would be prepared with a baffle centrally located to absorb the image of the source formed when a mirror is the gloss surface. Surrounding the centrally located baffle would be openings to pass any light which might be reflected by test specimens in directions adjacent to that of mirror reflection. Light reflected by surfaces in these adjacent directions indicates bloom of surfaces. Because the readings given with such a device would vary as the test surfaces varied in lightness and as the opening was changed

[16] Note that the values of $A_{45°,-45°}$ are apparent reflectances for 45° illumination and −45° viewing which are much greater than specular gloss values, $G_s(45°)$.

in shape, it seems safer to say that the reflectometer would compare otherwise similar surfaces for bloom rather than that it would measure them. A goniophotometer is needed for the latter task.

8. SHEEN, G_{sh}

A measure of sheen, G_{sh}, is merely a measure of specular gloss at a near-grazing angle, such as 75°. The device which is attached to the reflectometer for this measurement has been described above in section V, part 3. If values for the new angle are assigned to the standards for specular gloss at smaller angles, they may also be used as standards of sheen.

Papers and paper products have for many years been examined for gloss by inspection at near-grazing angles. It is not surprising therefore that an instrument which makes measurements at 75° is widely used in the paper industry [31]. In addition to interest in the sheen of papers, there is interest in the sheen of matte and semimatte paints, especially when these paints are to be used as interior finishes.

9. TRANSMISSION, T

It is possible, by merely turning each of the mirrors 7.5° in the attachment which measures sheen, to provide an attachment which measures transmission, T. Filters and clear solutions in glass-walled cells may be studied with this attachment. No material standard is needed, since comparisons may be made directly with the clear beam of the glass cell filled with the solvent used. Because it is sometimes possible to obtain filters of known spectral transmission when similarly measured opaque plaques are not available, transmission studies have, on occasion, been used to check the accuracy of the multipurpose instrument for tristimulus colorimetry and abridged spectrophotometry.

IX. SUMMARY

The design, construction, calibration, and use of a reflectometer having a wide variety of applications have been described. This multipurpose reflectometer is used to measure factors related to the appearance of ceramic products, paints, textile materials, papers, chemicals, and so on. The quantities most often evaluated are luminous apparent reflectance (indicative of lightness), trichromatic coefficients (indicative of chromaticity), and specular gloss (indicative of shininess). In addition, however, transmission, three other kinds of gloss, and abridged spectrophotometric values may be obtained with the apparatus.

The design of the reflectometer is based on the null principle. Light from a single source is directed along two separate paths. The beam reaching one cell is reflected specularly from one specimen; that reaching the second cell is reflected diffusely from the other. A galvanometer is used to indicate when the amounts of light in the beams have been adjusted so that each cell is generating the same current. By using the null method and beams which are geometrically different, a number of measuring operations are possible. However, the nonuniform photoelectric properties of manufactured barrier-layer photocells make it necessary to select from large groups of cells pairs which are suitable for use together in an instrument.

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Typical of the applications of the multipurpose reflectometer are the following: Measurement of the apparent reflectance, hiding power, and opacity of paints, papers, and porcelain enamels; measurement of the cleaning power of soaps and detergents; measurement of the magnitude and character of color difference between paint, cloth, ceramic, paper, or plastic samples of nearly the same color; measurement of whiteness, yellowing, fading, bleaching, blueing, and of tinting strength; determination of approximate spectral reflection curves; measurement of shininess of surfaces; classification of paints and other materials for specular gloss; measurement of luminous transmissions and approximate spectral transmissions of transparent solids and liquids. These last measurements are useful in chemical analyses.

When necessary precautions are taken, the multipurpose reflectometer may be made to operate with high precision; when proper standards are used and corrections applied, accurate results may be obtained. It is believed that the instrument will prove especially well suited for the measurement of small differences in lightness, color, and gloss between samples which are nearly identical.

X. REFERENCES

[1] Am. Soc. Testing Materials, *Tentative method of test for specular gloss of paint finishes*, 1939 Book of ASTM Tentative Standards.

[2] L. E. Barbrow, *A photometric procedure using barrier-layer photocells*. J. Research NBS **25,** (1940) RP 1348.

[3] B. T. Barnes, *A four-filter photoelectric colorimeter*, J. Opt. Soc. Am. **29,** 448 (1939).

[4] G. Becker and W. D. Appel, *Evaluation of manila-rope fiber for color*, BS J. Research **11,** 811 (1933) RP627.

[5] B. A. Brice, *A compensating circuit for blocking-layer photoelectric cells*, Rev. Sci. Instruments **8,** 279 (1937).

[6] Chicago Vitreous Enamel Product Co., *A new type photoelectric reflectometer*, Better Enameling, 1427 S. 55th Court, Chicago, Ill., **7,** No. 3, 12 (March, 1936).

[7] Corning Glass Works, Corning, N. Y., Pamphlet entitled, Glass Color Filters (1939).

[8] P. W. Cunliffe, *A method of producing standard artificially soiled wool fabric*, J. Textile Inst. **28,** T341 (1937).

[9] Eastman Kodak Co., Rochester, N. Y., Pamphlet entitled, Wratten Light Filters (1938).

[10] K. A. Evelyn, *A stabilized photoelectric colorimeter with light filters*, J. Biol. Chem. **115,** 63 (1936).

[11] Federal Standard Stock Catalog, Washington, D. C., Federal Specification TT–P–51a, *Paints; oil interior, . . . light-tints and white* (1937).

[12] Fish-Schurman Corp., 230 East 45th St., New York City, Pamphlet entitled, Jena Colored Optical Filter Glasses . . . (no date).

[13] G-M Laboratories, *Visitron self-generating cells*, G–M Comments, Jan., 1939, G–M Laboratories, Chicago, Ill.

[14] H. P. Gage, *Glass color filters for special applications*, J. Opt. Soc. Am. **27,** 159 (1937).

[15] H. A. Gardner, *Secondary standards for color*, Sci. Sec. Cir. 488, Nat. Paint, Varnish and Lacquer Assn., Washington, D. C. (1935).

[16] General Electric Co., Schenectady, N. Y., Drawing No. 496303 and accompanying blueprints describing three blocking-layer photocells (1935).

[17] General Electric Co., *The G–E light-sensitive cell*, Catalog GEA–2467 (1936); R. H. Mighell, *The light-sensitive cell*, G–E Review **40,** 372 (1937).

[18] K. S. Gibson, *Photoelectric photometers and colorimeters*, Instruments **9,** 309 and 335 (1936); National Bureau of Standards Letter Circular LC545, *Photoelectric colorimeters* (March 8, 1939).

[19] K. S. Gibson, *Spectral luminosity factors*, J. Opt. Soc. Am. **30,** 51 (1940).

[20] K. S. Gibson and H. J. Keegan, *On the magnitude of the error resulting from fluorescence in spectrophotometric measurements*, J. Opt. Soc. Am. **28,** 180 (1938).

[21] K. S. Gibson and G. K. Walker, *Standardization of railway signal glasses—Report No. 4, Chromaticities and luminous transmissions, . . .* Signal Section Proc., Amer. Railway Assoc. **30,** 420 (1933).
[22] I. H. Godlove, *Neutral value scales, II, . . .* J. Opt. Soc. Am. **23,** 419 (1933).
[23] A. C. Hardy, *A new recording spectrophotometer,* J. Opt. Soc. Am. **25,** 305 (1935); J. L. Michaelson, *Construction of the General Electric recording spectrophotometer,* J. Opt. Soc. Am. **28,** 365 (1938); and K. S. Gibson and H. J. Keegan, *Calibration and operation of the General Electric recording spectrophotometer of the National Bureau of Standards,* J. Opt. Soc. Am. **28,** 372 (1938).
[24] R. S. Hunter, *The glossmeter,* Sci. Sec. Circ. 456, Nat. Paint, Varnish and Lacquer Assn., Washington, D. C. (1934).
[25] R. S. Hunter, *A reflectometer and color comparator,* Sci. Sec. Cir. 461, Nat. Paint, Varnish and Lacquer Assn., Washington, D. C. (1934).
[26] R. S. Hunter, *A null method photoelectric reflectometer,* J. Opt. Soc. Am. **26,** 225 (1936).
[27] R. S. Hunter, *Methods of determing gloss,* J. Research NBS **18,** 19 (1937) RP958.
[28] R. S. Hunter, *Progress in developing a photoelectric method for measuring color difference,* Bul. Am. Ceram. Soc. **18,** 121 (1939).
[29] R. S. Hunter, *Photoelectric tristimulus colorimetry using one type of barrier-layer photocell.* [In preparation.]
[30] R. S. Hunter and D. B. Judd, *Development of a method of classifying paints according to gloss,* ASTM Bul. 97, 11 (March 1939).
[31] Institute of Paper Chemistry, *Instrumentation studies VI, The Modified Oxford glarimeter,* Paper Trade J. **104,** TS16 (1937).
[32] Institute of Paper Chemistry, *Instrumentation studies XIII, Adaptability of the G. E. reflection meter as a color analyzer,* Paper Trade J. **104,** TS245 (1937).
[33] Institute of Paper Chemistry, *Instrumentation Studies XXIX, A study of photoelectric instruments . . . Part V: The Hunter multi-purpose reflectometer,* Paper Trade J. **107,** TS275 (1938).
[34] L. A. Jones, *The gloss characteristics of photographic papers,* J. Opt. Soc. Am. **6,** 140 (1922).
[35] L. A. Jones, *Colorimetry: Preliminary draft of a report on nomenclature and definitions,* J. Opt. Soc. Am. **27,** 207 (1937).
[36] D. B. Judd, *The 1931 I. C. I. standard observer and coordinate system for colorimetry* J. Opt. Soc. Am. **23,** 359 (1933).
[37] D. B. Judd, *Optical specification of light-scattering materials,* J. Research, NBS **19,** 287 (1937) RP1026; [37a] Paper Trade J. **106,** TS5 (1938).
[38] D. B. Judd, *Opacity standards,* J. Research NBS **13,** 281 (1934) RP709.
[39] D. B. Judd, *Specification of uniform color tolerances for textiles,* Textile Research **9,** 253 (1939).
[40] L. Kenworthy and J. M. Waldram, *A reflectivity method for measuring the tarnishing of highly-polished metals,* J. Inst. Metals **55,** 247 (1934).
[41] B. Lange, Photoelements and Their Applications (Reinhold Pub. Corp., New York City, 1938).
[42] F. Lowenberg, 10 E. 40th St., New York City, Pamphlet entitled, Electrocell, Self-Generating Dry-Disc Photo-Electric Elements (1938).
[43] H. J. McNicholas, *Absolute methods in reflectometry,* BS J. Research **1,** 29 (1928) RP3.
[44] H. J. McNicholas, *Equipment for measuring the reflective and transmissive properties of diffusing media,* J. Research NBS **13,** 211 (1934) RP704.
[45] National Bureau of Standards, Letter Circular LC547, Preparation and Colorimetric Properties of a Magnesium-Oxide Reflectance Standard (1939).
[46] National Bureau of Standards, Commercial Standard CS62–38, Colors for Kitchen Accessories (1937).
[47] National Bureau of Standards, Commercial Standard CS63–38, Colors for Bathroom Accessories (1937).
[48] Pfaltz and Bauer, Inc., Empire State Bldg., New York City. Pamphle entitled, Photo-electric Cells and Apparatus (no date).
[49] Porcelain Enamel Institute, 612 N. Michigan Ave., Chicago, Ill. (Standard) Reflectance Test for Opaque White Porcelain Enamels (1937).
[50] Porcelain Enamel Institute, 612 N. Michigan Ave., Chicago, Ill. (Standard) Test for Acid Resistance of Porcelain Enamels (1937).

[51] Porcelain Enamel Institute, 612 N. Michigan Ave., Chicago, Ill. (Standard) Test for Resistance of Porcelain Enamels to Surface Abrasion (1938).
[52] Rubicon Co., Philadelphia, Pa., *Evelyn photoelectric colorimeter*, Bul. 460 (1937).
[53] F. Scofield, *Method of recording in definite percentages the fading of colors in paints and enamels*, Sci. Sec. Cir. 566, Nat. Paint, Varnish and Lacquer Assn., Washington, D. C. (1938).
[54] T. Smith and J. Guild, The C. I. E. colorimetric standards and their use, Trans. Opt. Soc. (London) **33,** 73 (1931), (see Resolution 3, p. 77 and 85).
[55] J. W. T. Walsh, Photometry (p. 104), Constable, London (1926).
[56] Westinghouse Electric and Mfg. Co., *Photox Cell—Type SW-30*, Catalog Section 43–705 (1935); E. D. Wilson, *A new light-sensitive device—the Photox*, Electric J. **32,** 270 (1935).
[57] Weston Electrical Instrument Corp., Newark, N. J. Pamphlet entitled, Technical Data on Weston Photoelectric Cells (1938).
[58] R. B. Withrow, C. L. Shrewsbury, and H. R. Kraybill, *The design of a precision photoelectric colorimeter*, Ind. Eng. Chem. (Anal. Ed.) **8,** 214 (1936).
[59] L. A. Wood, *A differential circuit for blocking-layer photocells*, Rev. Sci. Instr. **5,** 295 (1934).

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